Electronic Supplementary Material (ESI) for ChemComm.

Rh(III)-Catalyzed Synthesis of 1-Substituted Isoquinolinium Salts *via* C-H Bond Activation Reaction of Ketimines with Alkynes

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Supporting Information

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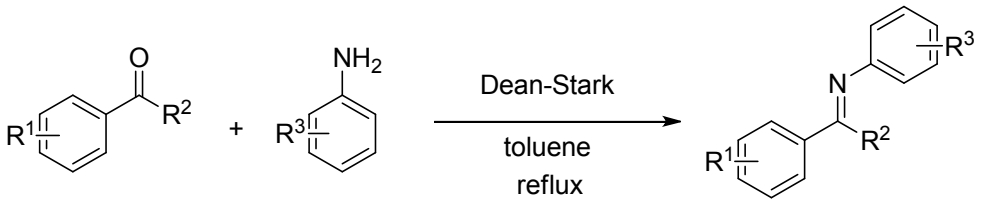
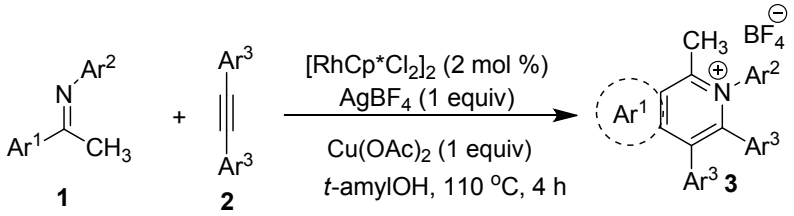
General. All reactions were conducted under a nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. All solvents were dried according to known methods and distilled prior to use.[1] All the imines were prepared from the corresponding ketones and amines according to the procedure known in the literature.[2]

General Procedure for the Synthesis of Ketoimines



A 100-mL two-neck round bottomed flask containing an equimolar amount of aromatic ketone (10.0 mmol) and aryl amine (10.0 mmol) and a magnetic stir bar was fitted with a Dean-Stark apparatus. To this reaction mixture was added 50 mL of dry toluene and the solution was refluxed with stirring for 15 h. Then the reaction solution was cooled and the solvent was removed under reduced pressure. The pure imines were obtained by recrystallization using ethanol.

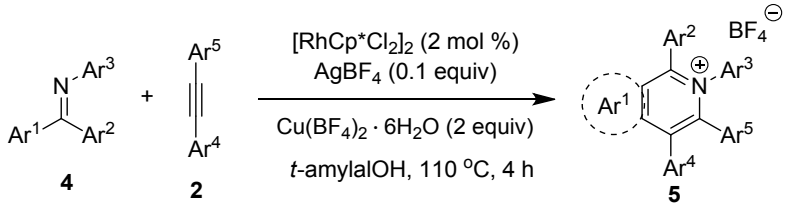
General Procedure for the Synthesis of Isoquinoline salts from Acetophenone imines.



A sealed tube containing $[RhCp^*Cl_2]_2$ (3.4 mg, 0.0056 mmol, 2.0 mol %), $AgBF_4$ (54.0 mg, 0.281 mmol), $Cu(OAc)_2$ (51.0 mg, 0.281 mmol), internal alkyne **2** (0.281 mmol) and acetophenone imine **1** (0.365 mmol) was evacuated and purged with nitrogen gas three times. Then, *t*-amylOH (2.0 mL) was added to the system via syringe under a nitrogen atmosphere and

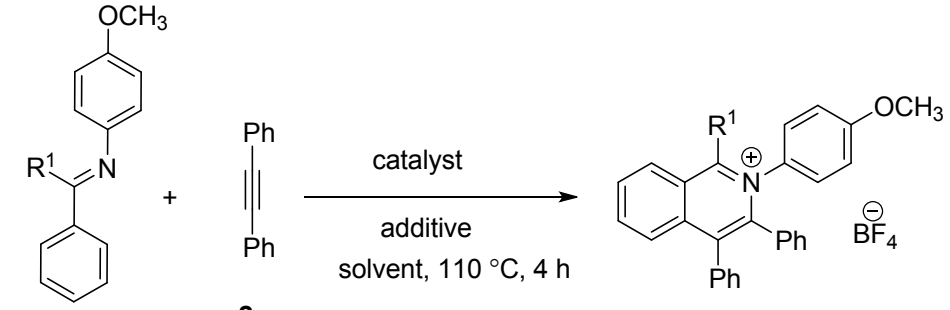
the reaction mixture was allowed to stir at 110 °C for 4 h. When the reaction was completed, the mixture was cooled and diluted with DCM (10 mL). The mixture was filtered through a Celite pad and the Celite pad was washed with DCM (40 mL) several times. The combined filtrate was concentrated in vacuo and the residue was purified by column chromatography using ethyl acetate/CH_3CN (1:1) to afford the desired product **3**.

General Procedure for the Synthesis of Isoquinoline salts from Benzophenone Imines.



A sealed tube containing $[RhCp^*Cl_2]_2$ (3.4 mg, 0.0056 mmol, 2.0 mol %), $AgBF_4$ (5.4 mg, 0.0281 mmol), $Cu(BF_4)_2$. $6H_2O$ (194.0 mg, 0.562 mmol), internal alkyne **2** (0.281 mmol) and benzophenone imine **4** (0.365 mmol) was evacuated and purged with nitrogen gas three times. Then, *t*-amylOH (2.0 mL) was added to the system *via* syringe under a nitrogen atmosphere and the reaction mixture was allowed to stir at 110 °C for 4 h. When the reaction was completed, the mixture was cooled and diluted with DCM (10 mL). The mixture was filtered through a Celite pad and the Celite pad was washed with DCM (40 mL) several times. The combined filtrate was concentrated in vacuo and the residue was dissolved in DCM (10 mL) and added drop wise to hexane (50 mL) under stirring to precipitate the salt products. The precipitate was filtered and recrystallized from DCM:hexane (1:5; 40 mL) to afford the desired product **3**.

Table 1. Optimization Study for Rhodium(III)-Catalyzed C-H Bond Activation of Acetophenone Imines[a] and Benzophenone Imines[b] with Diphenylacetylene



1a; $R^1 = CH_3$
4a; R^1 = Ph

2a

3a; $R^1 = CH_3$
5a; R^1 = Ph

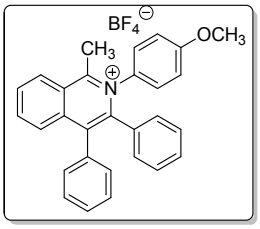
Entry	Catalyst	Solvent	Yield (%)[c]
1	$[RhCp^*Cl_2]_2$	*t*-amylOH	87[a]
2	$[RhCp^*Cl_2]_2$	EtOH	80[a]
3	$[RhCp^*Cl_2]_2$	MeOH	55[a]
4	$[RhCp^*Cl_2]_2$	DMF	0[a]
5	$[RhCp^*Cl_2]_2$	*O*-DCB	0[a]
6	$[RhCp^*Cl_2]_2$	DCE	0[a]
7	$[RhCp^*Cl_2]_2$	toluene	0[a]
8	$[RhCp^*Cl_2]_2$	1,4-dioxane	0[a]
9	$[RuCp^*Cl_2]_2$	*t*-amylOH	0[a]
10	$[Ru(p\text{-Cymene})Cl_2]_2$	*t*-amylOH	0[a]
11	$RhCl_3$	*t*-amylOH	0[a]
12	$PdCl_2(PhCN)_2$	*t*-amylOH	0[a]
13	$PdCl_2(CH_3CN)_2$	*t*-amylOH	0[a]
14	$[RhCp^*Cl_2]_2$	*t*-amylOH	95[b]

15	$[Ru(p\text{-Cymene})Cl_2]_2$	*t*-amylOH	81[d]
16	$[RhCp^*Cl_2]_2$	*t*-amylOH	97[e]
17	$[RhCp^*Cl_2]_2$	*t*-amylOH	37[f]
18		*t*-amylOH	0[a,g]
19		*t*-amylOH	0[b,g]

[a] Unless otherwise mentioned, all reactions were carried out using acetophenone imine **1a** (0.365 mmol), diphenyl acetylene **2a** (50.0 mg, 0.281 mmol), $[RhCp^*Cl_2]_2$ (3.4 mg, 0.00562 mmol, 2.0 mol %), $AgBF_4$ (54.0 mg, 0.281 mmol) and $Cu(OAc)_2$ (51.0 mg, 0.281 mmol) in *t*-amylOH (2.0 mL) at 110 ºC for 4 h. [b] Unless otherwise mentioned, all reactions were carried out using benzophenone imine **4a** (0.365 mmol), diphenyl acetylene **2a** (50 mg, 0.281 mmol), $[RhCp^*Cl_2]_2$ (3.4 mg, 0.00562 mmol), $AgBF_4$ (5.4 mg, 0.0281 mmol) and $Cu(BF_4)_2 \cdot 6H_2O$ (194.0 mg, 0.562 mmol) in *t*-amylOH at 110 ºC for 4 h. [c] Yields were determined by the ^1H NMR integration method using mesitylene as the internal standard. [d] Reaction was carried out using **4a** (0.365 mmol), **2a** (50.0 mg, 0.281 mmol), $[Ru(p\text{-Cymene})Cl_2]_2$ (3.4 mg, 0.00562 mmol) $AgBF_4$ (54.0 mg, 0.281 mmol) and $Cu(OAc)_2$ (51.0 mg, 0.281 mmol) in *t*-amylOH at 110 °C for 4 h. [e] Reaction was carried out using **4a** (0.365 mmol), diphenyl acetylene **2a** (50.0 mg, 0.281 mmol), $[RhCp^*Cl_2]_2$ (3.4 mg, 0.00562 mmol, 2.0 mol %), $AgBF_4$ (54.0 mg, 0.281 mmol) and $Cu(OAc)_2$ (51.0 mg, 0.281 mmol) in *t*-amylOH (2.0 mL) at 110 ºC for 4 h. [f] Reaction was carried out using **4a** (0.365 mmol), **2a** (50.0 mg, 0.281 mmol) and $Cu(BF_4)_2 \cdot 6H_2O$ (242.0 mg, 0.70 mmol) in *t*-amylOH at 110 °C for 4 h. [g] No $[RhCl_2Cp^*]_2$ catalyst was used.

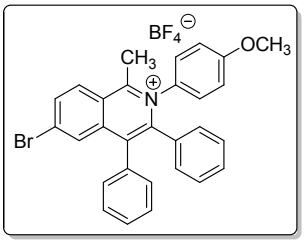
Spectral Data of Compounds 3 and 4

2-(4-Methoxyphenyl)-1-methyl-3,4-diphenylisoquinolin-2-ium tetrafluoroborate (3aa)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.59-8.56 (m, 1 H), 7.96-7.92 (m, 2 H), 7.69-7.67 (m, 1 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 7.28-7.22 (m, 5 H), 7.10-7.08 (m, 2 H), 6.96-6.94 (m, 3 H), 6.81 (d, *J* = 9.2 Hz, 2 H), 3.74 (s, 3 H), 3.00 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.8 (C), 160.1 (C), 145.2 (C), 137.9 (C), 137.1 (C), 136.3 (*C*H), 133.8 (C), 133.1 (C), 132.4 (C), 131.2 (2 *C*H), 130.7 (*C*H), 130.4 (2 *C*H), 128.9 (*C*H), 128.4 (3 *C*H), 128.1 (*C*H), 128.0 (2 *C*H), 127.4 (2 *C*H), 127.2 (*C*H), 127.1 (C), 114.6 (2 *C*H), 55.4 (O*C*H_3), 19.7 (*C*H_3); **HRMS** (FAB^+) cal for $C_{29}H_{24}NO$ 402.1852, found 402.1881; IR (neat): 3053, 1627, 1056 ($\nu_{B\text{-}F}$), 755 and 555 cm^{-1}.

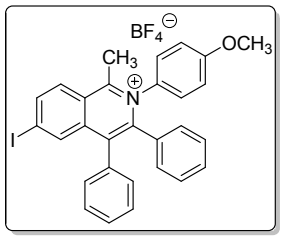
6-Bromo-2-(4-methoxyphenyl)-1-methyl-3,4-diphenylisoquinolin-2-iumtetrafluoroborate (3ba)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8.8 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.76 (s, 1 H), 7.31 (d, *J* = 8.8 Hz, 2 H), 7.24-7.22 (m, 5 H), 7.06-7.04 (m, 2 H), 6.93 (m, 3 H), 6.77 (d, *J* = 8.8 Hz, 2 H), 3.70 (s, 3 H), 2.99 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.9 (C), 160.2 (C), 145.2 (C), 137.9 (C), 137.2 (C), 136.4 (*C*H), 133.8 (C), 133.1 (C), 132.4 (C), 131.2 (2 *C*H), 130.8 (*C*H), 130.4 (2 *C*H), 128.9 (*C*H), 128.5 (2 *C*H), 128.2 (*C*H), 128.1 (2 *C*H), 127.7 (C), 127.5 (2 *C*H), 127.3 (*C*H), 127.1 (C), 114.6 (2 *C*H), 55.4 (O*C*H_3), 19.7 (*C*H_3); **HRMS** (FAB^+)

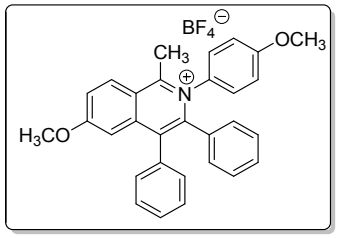
cal for $C_{29}H_{23}BrNO$ 480.0958, found 480.0964; IR (neat): 3053, 1615, 1056 ($\nu_{B\text{-}F}$), 755 and 550 cm^{-1}.

6-Iodo-2-(4-methoxyphenyl)-1-methyl-3,4-diphenylisoquinolin-2-iumtetrafluoroborate (3ca)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 8.4 Hz, 1 H), 7.92 (quin, *J* = 7.2 Hz, 2 H), 7.66 (d, *J* = 7.6 Hz, 1 H), 7.32 (d, *J* = 9.2 Hz, 2 H), 7.28-7.22 (m, 4 H), 7.07-7.02 (m, 2 H), 6.95-6.85 (m, 3 H), 6.80-6.74 (m, 2 H), 3.71 (s, 3 H), 2.99 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.9 (C), 160.2 (C), 145.3 (C), 138.0 (C), 137.2 (C), 136.4 (*C*H), 133.8 (C), 133.2 (C), 132.4 (C), 131.2 (2 *C*H), 130.8 (*C*H), 130.4 (2 *C*H), 130.3 (C), 128.9 (*C*H), 128.5 (2 *C*H), 128.2 (*C*H), 128.1 (2 *C*H), 127.5 (2 *C*H), 127.3 (*C*H), 127.2 (C), 114.7 (2 *C*H), 55.4 (O*C*H_3), 19.7 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{29}H_{23}INO$ 528.0819, found 528.0842; IR (neat): 2997, 1620, 1053 ($\nu_{B\text{-}F}$), 755 and 555 cm^{-1}.

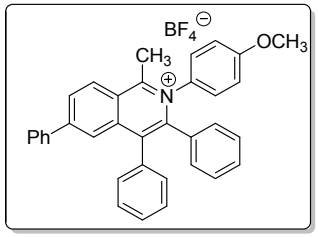
6-Methoxy-2-(4-methoxyphenyl)-1-methyl-3,4-diphenylisoquinolin-2-iumtetrafluoroborate (3da)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 9.6 Hz, 1 H), 7.50 (dd, *J* = 9.2 Hz, 2.4 Hz, 1 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 7.22 (m, 5 H), 7.04-7.03 (m, 2 H), 6.95-6.93 (m, 3 H), 6.83 (sd, *J* = 2.4 Hz, 1 H), 6.79 (d, *J* = 8.8 Hz, 2 H), 3.77 (s, 3 H), 3.72 (s, 3 H), 2.92 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9 (C), 160.1 (C), 158.7 (C), 145.5 (C), 141.1 (C), 135.3 (C),

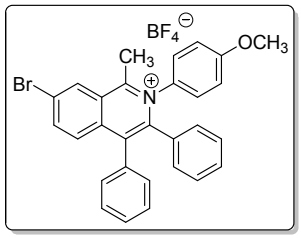
134.1 (C), 133.0 (C), 132.7 (C), 131.2 (*C*H), 131.1 (2 *C*H), 130.4 (2 *C*H), 128.8 (2 *C*H), 128.4 (*C*H), 128.3 (2 *C*H), 128.2 (*C*H), 127.5 (2 *C*H), 123.2 (*C*H), 122.4 (C), 114.6 (2 *C*H), 105.9 (*C*H), 55.9 (O*C*H_3), 55.5 (O*C*H_3), 19.5 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{30}H_{26}NO_2$ 432.1958, found 432.1964; IR (neat): 3062, 1627, 1056 ($\nu_{B\text{-}F}$), 750 and 555 cm^{-1}.

6-Phenyl-2-(4-methoxyphenyl)-1-methyl-3,4-diphenylisoquinolin-2-iumtetrafluoroborate (3ea)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 8.8 Hz, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 7.81 (s, 1 H), 7.54-7.53 (m, 2 H), 7.43-7.41 (m, 3 H), 7.34 (d, *J* = 8.8 Hz, 2 H), 7.26-7.24 (m, 5 H), 7.08-7.07 (m, 2 H), 6.97-6.95 (m, 3 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 3.72 (s, 3 H), 3.03 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.4 (C), 160.1 (C), 148.8 (C), 145.5 (C), 138.4 (C), 138.3 (C), 136.9 (C), 133.8 (C), 133.0 (C), 132.5 (C), 131.2 (2 *C*H), 130.4 (2 *C*H), 130.2 (*C*H), 129.7 (*C*H), 129.4 (*C*H), 129.1 (2 *C*H), 128.5 (2 *C*H), 128.4 (*C*H), 128.2 (2 *C*H, C), 127.7 (2 *C*H), 127.4 (2 *C*H), 126.1 (*C*H), 124.3 (*C*H), 114.6 (2 *C*H), 55.4 (O*C*H_3), 19.7 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{35}H_{28}NO$ 478.2165, found 478.2142; IR (neat): 3042, 1622, 1051 ($\nu_{B\text{-}F}$), 747 and 550 cm^{-1}.

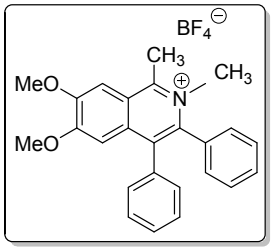
7-Bromo-2-(4-methoxyphenyl)-1-methyl-3,4-diphenylisoquinolin-2-iumtetrafluoroborate (3fa)



Brown solid; **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.74 (sd, *J* = 1.5 Hz, 1 H), 8.10-8.08 (m, 1 H), 7.60 (d, *J* = 9.0 Hz, 1 H), 7.29-7.22 (m, 7 H), 7.07-6.99 (m, 5 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 3.74

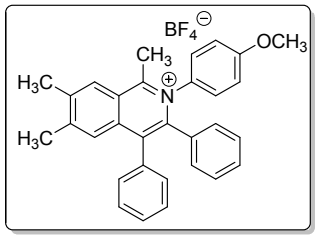
(s, 3 H), 2.98 (s, 3 H); **^{13}C NMR** (125 MHz, CD_2Cl_2): δ 160.9 (C), 160.4 (C), 146.4 (C), 140.2 (*C*H), 137.9 (C), 137.1 (C), 133.7 (C), 133.3 (C), 132.5 (C), 131.5 (2 *C*H), 131.0 (*C*H), 130.7 (2 *C*H), 129.4 (*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.7 (2 *C*H, C), 128.6 (2 *C*H), 127.9 (2 *C*H), 125.9 (C), 115.1 (2 *C*H), 55.9 (O*C*H_3), 20.3 (*C*H_3); **HRMS** (FAB^+) cal for $C_{29}H_{23}BrNO$ 480.0958, found 480.0953; IR (neat): 3053, 1627, 1056 ($\nu_{B\text{-}F}$), 755 and 555 cm^{-1}.

6,7-Dimethoxy-1,2-dimethyl-3,4-diphenylisoquinolin-2-iumtetrafluoroborate (**3ga**)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (s, 1 H), 7.27-7.24 (m, 6 H), 7.10-7.07 (m, 2 H), 6.72 (s, 1 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 4.89 (s, 3 H), 4.84 (s, 3 H), 3.76 (s, 3 H), 3.31 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.2 (C), 155.7 (C), 152.7 (C), 144.2 (C), 135.0 (C), 134.9 (C), 134.4 (C), 132.8 (C), 130.3 (2 *C*H), 130.2 (2 *C*H), 130.1 (*C*H), 128.7 (2 *C*H), 128.5 (2 *C*H), 128.4 (*C*H), 123.7 (C), 105.9 (*C*H), 104.9 (*C*H), 56.8 (O*C*H_3), 56.3 (O*C*H_3), 43.8 (*C*H_3), 18.2 (*C*H_3); **HRMS** (FAB^+) cal for $C_{25}H_{24}NO_2$ 370.1802, found 370.1806; IR (neat): 3051, 1611, 1055 ($\nu_{B\text{-}F}$), 750 and 555 cm^{-1}.

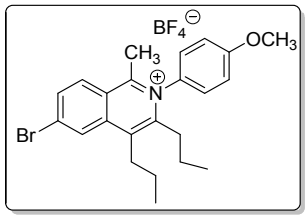
2-(4-Methoxyphenyl)-1,6,7-trimethyl-3,4-diphenylisoquinolin-2-iumtetrafluoroborate (**3ha**)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (s, 1 H), 7.41 (s, 1 H), 7.33 (d, *J* = 8.8 Hz, 2 H), 7.27-7.23 (m, 5 H), 7.07-7.05 (m, 2 H), 6.97-6.96 (m, 3 H), 6.83 (d, *J* = 9.2 Hz, 2 H), 3.75 (s, 3 H), 3.00 (s, 3 H), 2.57 (s, 3 H), 2.44 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.9 (C), 160.1 (C), 149.7 (C), 145.5 (C), 141.1 (C), 135.3 (C), 134.1 (C), 133.0 (C), 132.7 (C), 131.2 (*C*H),

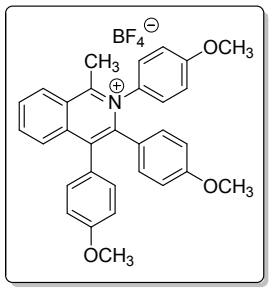
131.1 (2 *C*H), 130.4 (2 *C*H), 128.8 (2 *C*H), 128.4 (*C*H), 128.3 (2 *C*H), 128.2 (*C*H), 127.5 (2 *C*H), 123.2 (C), 122.4 (C), 114.6 (2 *C*H), 105.9 (*C*H), 55.9 (O*C*H_3), 19.5 (2 *C*H_3), 19.4 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{31}H_{28}NO$ 430.2165, found 430.2162; IR (neat): 3055, 1627, 1056 ($\nu_{B\text{-}F}$), 750 and 552 cm^{-1}.

6-Bromo-2-(4-methoxyphenyl)-1-methyl-3,4-dipropylisoquinolin-2-iumtetrafluoroborate (3bb)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.8 Hz, 1 H), 8.23 (s, 1 H), 7.87 (d, *J* = 9.2 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 7.12 (d, *J* = 8.8 Hz, 2 H), 3.89 (s, 3 H), 3.02-2.98 (m, 2 H), 2.77 (s, 3 H), 2.64 (d, *J* = 8.0 Hz, 2 H), 1.77-1.71 (m, 2 H), 1.58-1.45 (m, 2 H), 1.13 (t, *J* = 7.2 Hz, 3 H), 0.75 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.1 (C), 160.5 (C), 147.2 (C), 138.1 (C), 133.6 (*C*H), 133.3 (C), 132.8 (C), 132.3 (C), 131.2 (2 *C*H), 127.3 (2 *C*H), 126.6 (*C*H), 125.1 (C), 115.7 (2 *C*H), 55.8 (O*C*H_3), 33.2 (*C*H_2), 30.7 (*C*H_2), 23.7 (*C*H_2), 22.9 (*C*H_2), 19.8 (*C*H_3), 14.5 (*C*H_3), 14.3 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{23}H_{27}BrNO$ 412.1271, found 412.1267; IR (neat): 3053, 2972, 1627, 1055 ($\nu_{B\text{-}F}$), 755 and 550 cm^{-1}.

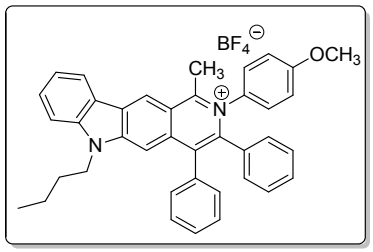
2,3,4-Tris(4-methoxyphenyl)-1-methylisoquinolin-2-iumtetrafluoroborate (3ac)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.4 Hz, 1 H), 7.94-7.86 (m, 2 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.27 (d, *J* = 8.8 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H),

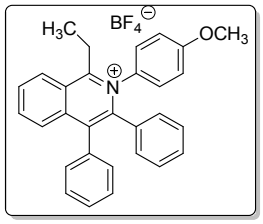
6.81 (d, J = 8.8 Hz, 2 H), 6.75 (d, J = 8.4 Hz, 2 H), 6.46 (d, J = 8.4 Hz, 2 H), 3.73 (s, 6 H), 3.59 (s, 3 H), 2.96 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.4 (C), 160.1 (C), 159.4 (C), 159.1 (C), 145.7 (C), 138.1 (C), 137.3 (C), 136.1 (*C*H), 134.0 (C), 132.2 (2 *C*H), 132.1 (2 *C*H), 131.3 (*C*H), 129.7 (*C*H), 129.4 (2 *C*H), 129.3 (*C*H), 129.2 (C), 128.5 (C), 124.2 (C), 114.6 (2 *C*H), 113.6 (2 *C*H), 112.7 (2 *C*H), 55.9 (O*C*H_3), 55.6 (O*C*H_3), 55.5 (O*C*H_3), 19.7 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{31}H_{28}NO_3$ 462.2064, found 462.2042; IR (neat): 3047, 1620, 1057 ($\nu_{B\text{-}F}$), 752 and 555 cm^{-1}.

6-Butyl-2-(4-methoxyphenyl)-1-methyl-3,4-diphenyl-6H-pyrido[4,3-b]carbazol-2-ium tetrafluoroborate (**3ia**)



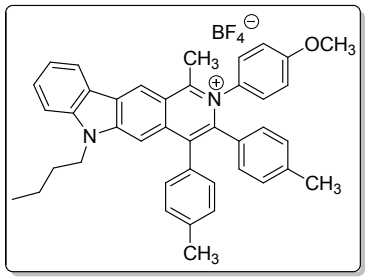
Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.32 (s, 1 H), 8.35 (s, 1 H), 7.60 (t, J = 7.2 Hz, 2 H), 7.31-7.24 (m, 8 H), 7.08-7.07 (m, 2 H), 6.98-6.97 (m, 2 H), 6.96-6.93 (m, 2 H), 6.81 (d, J = 8.0 Hz, 2 H), 4.05-4.03 (m, 2 H), 3.73 (s, 3 H), 3.16 (s, 3 H), 1.74-1.67 (m, 2 H), 1.25-1.16 (m, 2 H), 0.97-0.78 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.9 (C), 159.5 (C), 145.9 (C), 143.1 (C), 142.3 (C), 135.8 (C), 134.9 (C), 134.6 (C), 133.2 (C), 133.0 (C), 131.4 (2 *C*H), 130.5 (2 *C*H), 129.3 (*C*H), 128.8 (2 *C*H), 128.7 (C), 128.2 (*C*H), 128.1 (2 *C*H), 128.0 (*C*H), 127.4 (2 *C*H), 122.6 (*C*H), 121.8 (C), 121.7 (*C*H), 121.4 (*C*H), 120.2 (C), 114.6 (2 *C*H), 109.2 (*C*H), 102.8 (*C*H), 55.4 (O*C*H_3), 42.7 (*C*H_2), 30.1 (*C*H_2), 20.0 (*C*H_3), 19.9 (*C*H_2), 13.4 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{39}H_{35}N_2O$ 547.2744, found 547.2742; IR (neat): 3051, 1631, 1056 ($\nu_{B\text{-}F}$), 755 and 557 cm^{-1}.

1-Ethyl-2-(4-methoxyphenyl)-3,4-diphenylisoquinolin-2-ium tetrafluoroborate (**3ka**)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.59-8.56 (m, 1 H), 7.99-7.96 (m, 2 H), 7.73-7.71 (m, 1 H), 7.40 (d, *J* = 8.8 Hz, 2 H), 7.31-7.23 (m, 7 H), 7.11-7.09 (m, 1 H), 6.97-6.96 (m, 2 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 3.75 (s, 3 H), 3.45-3.43 (m, 2 H), 1.43 (t, *J* = 7.4 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.0 (C), 160.3 (C), 145.1 (C), 138.5 (C), 137.5 (C), 136.4 (*C*H), 133.8 (C), 133.1 (C), 132.4 (C), 131.2 (2 *C*H), 130.9 (2 *C*H), 130.4 (2 *C*H), 128.6 (2 *C*H), 128.5 (2 *C*H), 128.2 (*C*H), 127.8 (*C*H), 127.5 (2 *C*H), 127.2 (*C*H), 126.2 (C), 114.4 (2 *C*H), 55.5 (O*C*H_3), 25.7 (*C*H_2), 14.6 (*C*H_3); **HRMS** (FAB^+) cal for $C_{30}H_{26}NO$ 416.2009, found 416.2020; IR (neat): 3051, 1631, 1052 ($\nu_{B\text{-}F}$), 755 and 555 cm^{-1}.

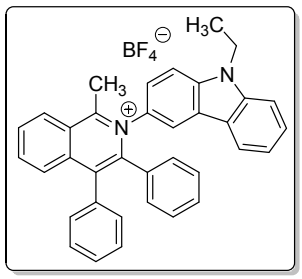
6-Butyl-2-(4-methoxyphenyl)-1-methyl-3,4-di-*p*-tolyl-6H-pyrido[4,3-b]carbazol-2-ium tetrafluoroborate (**3ic**)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.34 (s, 1 H), 8.39 (d, *J* = 6.8 Hz, 1 H), 7.61 (t, *J* = 7.2 Hz, 2 H), 7.45-7.38 (m, 2 H), 7.36-7.26 (m, 3 H), 7.16-7.05 (m, 4 H), 6.90 (d, *J* = 7.6 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 6.77 (d, *J* = 8.0 Hz, 2 H), 4.12 (t, *J* = 6.8 Hz, 2 H), 3.76 (s, 3 H), 3.12 (s, 3 H), 2.32 (s, 3 H), 2.26 (s, 3 H), 1.79-1.67 (m, 2 H), 1.36-1.22 (m, 2 H), 0.82 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.9 (C), 159.3 (C), 145.9 (C), 143.2 (C), 142.5 (C),

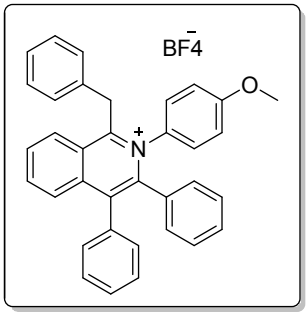
137.9 (C), 137.7 (C), 136.1 (C), 134.8 (C), 133.3 (C), 131.9 (C), 131.1 (2 *C*H), 130.3 (2 *C*H), 130.1 (C), 129.3 (*C*H), 128.9 (2 *C*H), 128.8 (2 *C*H), 128.7 (*C*H), 128.2 (2 *C*H), 122.6 (*C*H), 121.9 (*C*H), 121.7 (C), 121.5 (C), 120.2 (C), 114.2 (2 *C*H), 109.3 (*C*H), 102.9 (*C*H), 55.5 (O*C*H_3), 42.8 (*C*H_2), 30.2 (*C*H_2), 21.2 (*C*H_3), 21.1 (*C*H_2), 20.1 (2 *C*H_3), 13.4 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{41}H_{39}N_2O$ 575.3057, found 575.3061; IR (neat): 3050, 1627, 1056 ($\nu_{B\text{-}F}$), 747 and 557 cm^{-1}.

2-(9-Ethyl-9*H*-carbazol-3-yl)-1-methyl-3,4-diphenylisoquinolin-2-iumtetrafluoroborate (3ja)



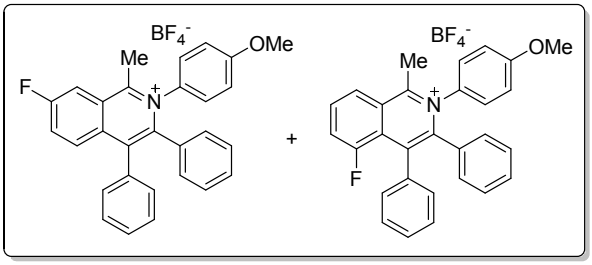
Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 8.0 Hz, 1 H), 8.12 (s, 1 H), 8.07 (d, *J* = 7.6 Hz, 1 H), 7.96 (t, *J* = 7.6 Hz, 2 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 7.52-747 (m, 4 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.32-7.30 (m, 5 H), 7.16 (d, *J* = 7.2 Hz, 1 H), 7.10 (m, 1 H), 6.89 (m, 1 H), 6.81-6.80 (m, 2 H), 4.30 (t, *J* = 7.2 Hz, 2 H), 3.05 (s, 3 H), 1.47-1.35 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.2 (C), 145.7 (C), 140.7 (C), 139.5 (C), 138.0 (C), 137.2 (C), 136.3 (*C*H), 133.9 (C), 132.5 (C), 132.0 (C), 131.3 (*C*H), 131.2 (*C*H), 130.8 (*C*H), 130.7 (*C*H), 130.4 (*C*H), 128.9 (*C*H), 128.3 (2 *C*H), 128.2 (2 *C*H), 128.1 (*C*H), 127.5 (2 *C*H), 127.4 (2 *C*H), 127.2 (C), 127.0 (*C*H), 124.2 (*C*H), 123.0 (C), 122.2 (C), 121.2 (*C*H), 119.9 (*C*H), 119.3 (*C*H), 37.8 (*C*H_2), 20.1 (*C*H_3), 13.7 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{36}H_{29}N_2$ 439.2325, found 439.2322; IR (neat): 3051, 1630, 1052 ($\nu_{B\text{-}F}$), 750 and 557 cm^{-1}.

1-Benzyl-2-(4-methoxyphenyl)-3,4-diphenylisoquinolin-2-ium (3la)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.8 Hz, 1 H), 7.96 (t, *J* = 8.4 Hz, 1 H), 7.86 (t, *J* = 8.4 Hz, 1 H), 7.75 (d, *J* = 10.0 Hz, 1 H), 7.33-7.09 (m, 12 H), 6.95-6.88 (m, 5 H), 6.61 (d, *J* = 10.0 Hz, 2 H), 4.89 (s, 2 H), 3.69 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.9 (C), 160.0 (C), 146.0 (C), 138.7 (C), 138.2 (C), 136.4 (C), 135.8 (C), 133.7 (C), 132.4 (C), 132.3 (C), 131.1 (2 *C*H), 131.0 (*C*H), 130.4 (2 *C*H), 129.3 (*C*H), 129.0 (2 *C*H), 128.6 (2 *C*H), 128.4 (*C*H), 128.2 (*C*H), 128.1 (2 *C*H), 127.9 (2 *C*H), 127.5 (2 *C*H), 127.4 (2 *C*H), 127.3 (*C*H), 114.0 (2 *C*H), 55.4 (CH_3), 37.6 (CH_2); **HRMS** (FAB^+) cal for $C_{35}H_{28}NO^+$ 478.2165, found 478.2170; IR (neat): 3042, 1622, 1056 ($\nu_{B\text{-}F}$), 755 and 550 cm^{-1}.

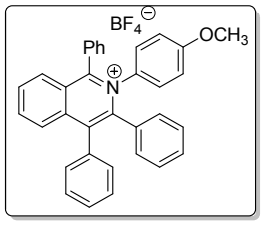
7-Fluoro-2-(4-methoxyphenyl)-1-methyl-3,4-diphenylisoquinolin-2-ium (3ma) and 5-Fluoro-2-(4-methoxyphenyl)-1-methyl-3,4-diphenylisoquinolin-2-ium (3ma′)



Brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.4 Hz, 1 H), 8.07 (d, *J* = 6.8 Hz, 1 H), 7.85-7.80 (m, 1 H), 7.67-6.51 (m, 2 H), 7.34-7.17 (m, 8 H), 7.11-7.01 (m, 7 H), 6.90-6.83 (m, 5 H), 6.75-6.72 (m, 3 H), 3.70 (s, 3 H), 3.66 (s, 3 H), 2.93 (s, 3 H), 2.88 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.1 (C), 160.0 (CH), 159.4 (*C*), 156.8 (C), 146.4 (C), 136.1 (C), 135.2 (C), 133.6 (C), 133.2 (*C*H), 132.2 (*C*), 132.0 (*C*H), 131.2 (3 *C*H), 131.1 (*C*H), 130.5 (*C*), 130.3 (*C*H), 129.3 (2 *C*H), 128.7 (*C*), 128.5 (3 *C*H), 128.4 (*C*H), 128.3 (CH), 127.5 (2 *C*H), 127.4 (CH),

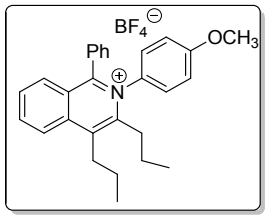
127.3 (3 *C*H), 127.1 (3 *C*H), 126.2 (d_F, *J* = 25.0 Hz, *C*), 125.5 (CH), 121.9 (d_F, *J* = 22.0 Hz, *C*H), 114.4 (3 *C*H), 112.4 (d_F, *J* = 23.5 Hz, *C*), 55.3 (2 O*C*H$_3$), 20.4 (*C*H$_3$), 19.8 (*C*H$_3$); **HRMS** (FAB$^+$) cal for $C_{29}H_{23}NO_2^+$ 420.1758, found 420.1768; IR (KBr): 3062, 1627, 1573, 1388 and 1056 ($\nu_{B\text{-}F}$), 753, 557 cm^{-1}.

2-(4-Methoxyphenyl)-1,3,4-triphenylisoquinolin-2-iumtetrafluoroborate (5aa)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00-7.96 (m, 1 H), 7.84-7.75 (m, 3 H), 7.57-7.55 (m, 2 H), 7.43-7.36 (m, 6 H), 7.31-7.21 (m, 6 H), 6.98-6.96 (m, 3 H), 6.49 (d, *J* = 8.8 Hz, 2 H), 3.58 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.7 (C), 159.3 (C), 145.8 (C), 139.2 (C), 138.8 (C), 136.4 (*C*H), 133.9 (C), 133.4 (C), 132.4 (C), 131.3 (2 *C*H), 131.2 (*C*H), 130.9 (C), 130.5 (2 *C*H), 130.4 (*C*H), 130.3 (2 *C*H), 130.0 (*C*H), 129.7 (2 *C*H), 128.4 (*C*H), 128.3 (2 *C*H), 128.2 (*C*H), 128.1 (2 *C*H), 127.9 (C), 127.4 (2 *C*H), 127.0 (*C*H), 113.4 (2 *C*H), 55.2 (O*C*H$_3$); EI mass cal for $C_{34}H_{26}NO$ 464.2009, found 464.2; IR (neat): 3051, 1622, 1055 ($\nu_{B\text{-}F}$), 750 and 557 cm^{-1}.

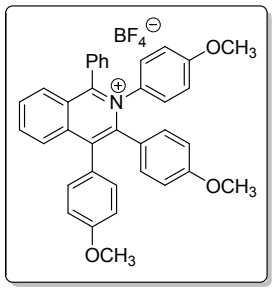
2-(4-Methoxyphenyl)-1-phenyl-3,4-dipropylisoquinolin-2-ium tetrafluoroborate (5ab)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.8 Hz, 1 H), 8.06 (d, *J* = 7.6 Hz, 1 H), 7.64 (d, *J* = 7.6 Hz, 2 H), 7.56 (d, *J* = 8.8 Hz, 2 H), 7.31-7.24 (m, 5 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 3.72 (s, 3 H), 3.19-3.16 (m, 2 H), 2.80-2.75 (m, 2 H), 1.85-1.78 (m, 2 H), 1.58-1.52 (m, 2 H), 1.24-1.15 (m, 3 H), 0.93-0.75 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.3 (C), 159.7 (C), 146.8 (C), 138.5 (C), 136.7 (C), 136.6 (*C*H), 133.3 (C), 131.5 (*C*H), 130.9 (C), 130.0 (2 *C*H), 129.9 (2 *C*H), 128.8 (2 *C*H), 128.2 (2 *C*H), 127.0 (C), 124.0 (*C*H), 114.3 (2 *C*H), 55.5 (O*C*H$_3$),

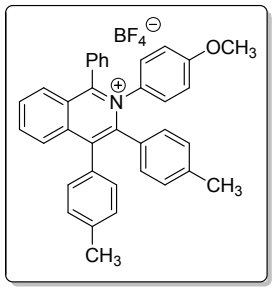
33.1 (*C*H_2), 31.1 (*C*H_2), 23.7 (*C*H_2), 22.9 (*C*H_2), 14.7 (*C*H_3), 14.4 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{28}H_{30}NO$ 396.2322, found 396.2333; IR (neat): 3051, 1631, 1056 ($\nu_{B\text{-}F}$), 755 and 557 cm^{-1}.

2,3,4-Tris(4-methoxyphenyl)-1-phenylisoquinolin-2-ium tetrafluoroborate (**5ac**)



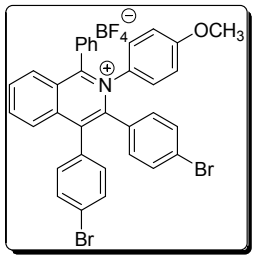
Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.2 Hz, 1 H), 7.79-7.68 (m, 3 H), 7.50-7.48 (m, 2 H), 7.33-7.32 (m, 3 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 6.77 (d, *J* = 8.4 Hz, 2 H), 6.45 (d, *J* = 8.0 Hz, 4 H), 3.73 (s, 3 H), 3.56 (s, 3 H), 3.54 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.4 (C), 159.3 (C), 159.2 (C), 159.0 (C), 146.2 (C), 139.7 (C), 139.1 (C), 136.3 (*C*H), 133.6 (C), 132.7 (2 *C*H), 131.8 (2 *C*H), 131.1 (2 *C*H), 130.2 (2 *C*H, C), 130.0 (*C*H), 129.7 (2 *C*H), 128.2 (2 *C*H), 127.8 (C), 127.1 (*C*H), 126.3 (C), 124.8 (C), 113.7 (2 *C*H), 113.5 (2 *C*H), 113.0 (2 *C*H), 55.2 (O*C*H_3), 55.1 (O*C*H_3), 54.9 (O*C*H_3); **HRMS** (FAB$^+$) cal for $C_{36}H_{30}NO_3$ 524.2220, found 524.2227; IR (neat): 3053, 1631, 1056 ($\nu_{B\text{-}F}$), 752 and 557 cm^{-1}.

2-(4-Methoxyphenyl)-1-phenyl-3,4-di-p-tolylisoquinolin-2-ium tetrafluoroborate (5ad)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (t, *J* = 8.2 Hz, 1 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.93-7.89 (m, 1 H), 7.72-7.70 (m, 2 H), 7.54-7.50 (m, 3 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.38 (d, *J* = 9.2 Hz, 2 H), 7.26 (t, *J* = 7.6 Hz, 4 H), 6.92 (d, *J* = 8.0 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 3.74 (s, 3 H), 2.48 (s, 3 H), 2.26 (s, 3 H); **^{13}C NMR** (125 MHz, CD_2Cl_2): δ 160.9 (C), 159.8 (C), 146.3 (C), 139.7 (C), 139.3 (C), 138.9 (C), 138.6 (C), 136.9 (*C*H), 133.6 (C), 131.4 (2 *C*H), 131.4 (*C*H), 131.2 (C), 130.9 (*C*H), 130.6 (2 *C*H), 130.4 (3 *C*H), 129.9 (2 *C*H), 129.8 (C), 129.2 (2 *C*H), 128.6 (2 *C*H), 128.5 (2 *C*H, C), 128.0 (C), 127.2 (*C*H), 113.7 (2 *C*H), 55.5 (O*C*H_3), 21.3 (*C*H_3), 21.2 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{36}H_{30}NO$ 492.2322, found 492.2334; IR (neat): 3050, 1617, 1056 ($\nu_{B\text{-}F}$), 750 and 552 cm^{-1}.

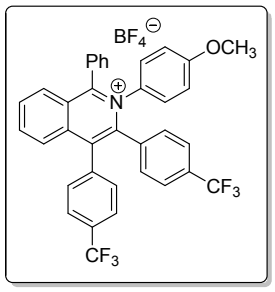
2-(4-Methoxyphenyl)-1-phenyl-3,4-di-p-bromophenylisoquinolin-2-iumtetrafluoroborate (5ae)



Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.11-8.08 (m, 1 H), 7.89-7.88 (m, 2 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 7.54-7.41 (m, 8 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.24-7.16 (m, 5 H), 6.57 (d, *J* = 8.4 Hz, 2 H), 3.58 (s, 3 H); **^{13}C NMR** (125 MHz, CD_2Cl_2): δ 161.9 (C), 160.1 (C), 144.8 (C), 139.3 (C), 138.1 (C), 137.4 (*C*H), 133.4 (C), 133.3 (2 *C*H), 132.5 (2 *C*H), 132.0 (2 *C*H), 131.8 (*C*H), 131.6 (C), 131.3 (2 *C*H), 131.2 (*C*H), 131.0 (C), 130.7 (*C*H), 130.5 (2 *C*H), 130.2 (C), 129.9 (2

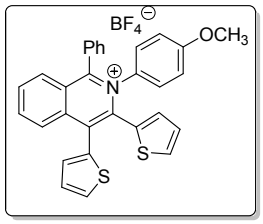
*C*H), 128.7 (2 *C*H), 128.4 (C), 126.9 (*C*H), 123.8 (C), 123.3 (C), 114.0 (2 *C*H), 55.7 (O*C*H$_3$); **HRMS** (FAB$^+$) cal for $C_{34}H_{24}Br_2NO$ 620.0219, found 620.0241; IR (neat): 3052, 1631, 1055 ($\nu_{B\text{-}F}$), 755 and 557 cm^{-1}.

2-(4-Methoxyphenyl)-1-phenyl-3,4-bis(4-(trifluoromethyl)phenyl)isoquinolin-2-ium tetrafluoroborate (5af)



Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.10-8.09 (m, 1 H), 7.90 (m, 2 H), 7.78 (d, *J* = 7.6 Hz, 1 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.60 (m, 4 H), 7.53-7.50 (m, 2 H), 7.43-7.42 (m, 4 H), 7.27 (d, *J* = 7.6 Hz, 2 H), 7.22 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 8.8 Hz, 2 H), 3.58 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.4 (C), 160.3 (C), 144.4 (C), 139.1 (C), 137.9 (C), 137.7 (*C*H), 136.2 (C), 133.2 (C), 132.7 (C), 132.3 (2 *C*H), 132.0 (*C*H), 131.5 (4 *C*H), 131.2 (C), 131.1 (C), 130.9 (*C*H), 130.8 (C), 130.5 (2 *C*H), 130.3 (C), 130.0 (2 *C*H), 128.8 (2 *C*H), 128.6 (C), 128.5 (C), 126.9 (*C*H), 125.8 (2 *C*H), 125.0 (*C*H), 114.1 (2 *C*H), 55.7 (O*C*H$_3$); **HRMS** (FAB$^+$) cal for $C_{36}H_{24}F_6NO$ 600.1757, found 600.1742; IR (neat): 3047, 1632, 1056 ($\nu_{B\text{-}F}$), 750 and 557 cm^{-1}.

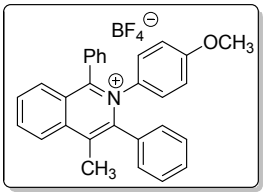
2-(4-Methoxyphenyl)-1-phenyl-3,4-di(thiophen-2-yl)isoquinolin-2-iumtetrafluoroborate (5ag)



Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.14-8.10 (m, 1 H), 7.90 (d, *J* = 8.0 Hz, 2 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.53 (d, *J* = 7.6 Hz, 4 H), 7.49-7.43 (m, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H),

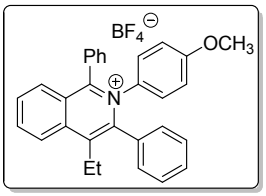
7.24-7.16 (m, 5 H), 6.59 (d, J = 8.8 Hz, 2 H), 3.65 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.9 (C), 160.2 (C), 144.8 (C), 139.3 (C), 138.1 (C), 137.5 (*C*H), 133.1 (2 *C*H), 132.5 (2 *C*H), 132.1 (2 *C*H), 131.8 (*C*H), 131.6 (C), 131.3 (2 *C*H), 131.0 (C), 130.7 (*C*H), 130.5 (2 *C*H), 129.9 (2 *C*H), 128.7 (2 *C*H), 128.4 (C), 127.0 (*C*H), 123.8 (C), 123.4 (C), 114.1 (2 *C*H), 55.7 (O*C*H$_3$); EI mass cal for $C_{30}H_{22}NOS_2$ 476.1137, found 476.2; IR (neat): 3051, 1622, 1056 ($\nu_{B\text{-}F}$), 750 and 550 cm^{-1}.

4-Methyl-2-(4-methoxyphenyl)-1,3-diphenylisoquinolin-2-ium tetrafluoroborate (5ah)



Brown solid; **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 8.42 (d, J = 9.0 Hz, 1 H), 8.27-8.23 (m, 1 H), 7.89-7.86 (m, 1 H), 7.82 (d, J = 8.5 Hz, 1 H), 7.43-7.26 (m, 11 H), 7.01-6.99 (m, 2 H), 6.54-6.52 (m, 2 H), 3.59 (s, 3 H), 2.61 (s, 3 H); **^{13}C NMR** (125 MHz, CD_2Cl_2): δ 160.0 (C), 145.9 (C), 139.2 (C), 137.6 (*C*H), 134.3 (C), 133.5 (C), 132.9 (C), 132.1 (*C*H), 131.3 (*C*H), 130.9 (2 *C*H), 130.7 (*C*H), 130.5 (2 *C*H), 130.3 (C), 130.1 (C), 129.8 (2 *C*H), 128.9 (2 *C*H), 128.8 (2 *C*H), 125.2 (*C*H), 115.3 (C), 113.9 (2 *C*H), 55.7 (O*C*H$_3$), 16.9 (*C*H$_3$); **HRMS** (FAB$^+$) cal for $C_{29}H_{24}NO$ 402.1852, found 402.1855; IR (neat): 3051, 1631, 1056 ($\nu_{B\text{-}F}$), 755 and 557 cm^{-1}.

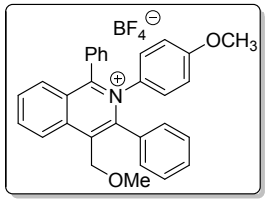
4-Ethyl-2-(4-methoxyphenyl)-1,3-diphenylisoquinolin-2-iumtetrafluoroborate (5ai)



Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.38 (d, J = 8.4 Hz, 1 H), 8.18-8.15 (m, 1 H), 7.78-7.77 (m, 2 H), 7.45 (d, J = 7.6 Hz, 2 H), 7.39-7.33 (m, 5 H), 7.27-7.26 (m, 3 H), 7.13 (d, J = 8.4 Hz, 2 H), 6.48 (d, J = 8.4 Hz, 2 H), 3.75 (s, 3 H), 2.99-2.96 (m, 2 H), 1.30 (t, J = 7.6 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.5 (C), 159.2 (C), 145.3 (C), 138.8 (C), 138.0 (C), 136.6

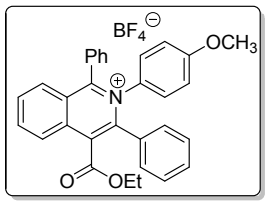
(*C*H), 133.3 (C), 132.3 (C), 131.8 (C), 130.7 (C), 130.5 (2 *C*H), 130.2 (*C*H), 130.1 (2 *C*H), 129.8 (*C*H), 129.5 (*C*H), 129.1 (*C*H), 128.2 (2 *C*H), 128.1 (2 *C*H), 124.5 (*C*H), 55.1 (O*C*H$_3$), 23.2 (*C*H$_2$), 14.4 (*C*H$_3$); **HRMS** (FAB$^+$) cal for $C_{30}H_{26}NO$ 416.2009, found 416.2012; IR (neat): 3032, 1631, 1056 ($\nu_{B\text{-}F}$), 755 and 555 cm^{-1}.

4-(Methoxymethyl)-2-(4-methoxyphenyl)-1,3-diphenylisoquinolin-2-ium tetrafluoroborate (5aj)



Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.52 (d, *J* = 8.8 Hz, 1 H), 8.16-8.12 (m, 1 H), 7.79-7.73 (m, 2 H), 7.43-7.39 (m, 5 H), 7.35-7.32 (m, 3 H), 7.30-7.23 (m, 2 H), 7.11-7.07 (m, 2 H), 6.49-6.45 (m, 2 H), 4.60 (s, 2 H), 3.48 (s, 3 H), 3.23 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.8 (C), 159.3 (C), 146.9 (C), 138.8 (C), 137.0 (*C*H), 133.1 (C), 132.2 (C), 131.6 (*C*H), 131.5 (C), 130.9 (2 *C*H), 130.6 (C), 130.5 (*C*H), 130.1 (*C*H), 130.0 (2 *C*H), 129.6 (2 *C*H), 129.5 (*C*H), 128.2 (2 *C*H), 128.0 (2 *C*H), 127.9 (C), 125.5 (*C*H), 113.4 (2 *C*H), 68.4 (*C*H$_2$), 58.6 (O*C*H$_3$), 55.2 (O*C*H$_3$); **HRMS** (FAB$^+$) cal for $C_{30}H_{26}NO_2$ 432.1958, found 432.1942; IR (neat): 3051, 2972, 1631, 1052 ($\nu_{B\text{-}F}$), 755 and 557 cm^{-1}.

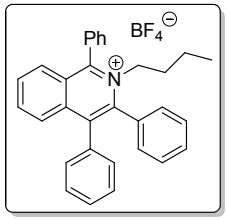
4-(Ethoxycarbonyl)-2-(4-methoxyphenyl)-1,3-diphenylisoquinolin-2-ium tetrafluoroborate (5ak)



Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.21 (m, 2 H), 7.85 (m, 2 H), 7.50 (m, 2 H), 7.43-7.39 (m, 6 H), 7.26-7.24 (m, 2 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 6.54 (d, *J* = 8.0 Hz, 2 H), 4.16-4.13 (m, 2 H), 3.61 (s, 3 H), 0.90 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.2 (CO),

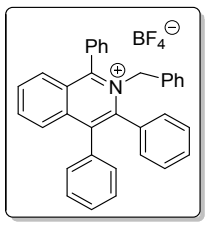
163.2 (C), 159.7 (C), 145.2 (C), 138.1 (*C*H), 135.5 (C), 132.2 (C), 131.9 (*C*H), 131.4 (*C*H), 131.1 (C), 130.8 (2 *C*H), 130.5 (*C*H), 130.2 (C), 130.1 (2 *C*H), 129.8 (*C*H), 129.6 (2 *C*H), 128.7 (C), 128.6 (C), 128.4 (2 *C*H), 128.0 (2 *C*H), 125.3 (*C*H), 113.7 (2 *C*H), 62.8 (O*C*H_2), 55.3 (O*C*H_3), 13.4 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{31}H_{26}NO_3$ 460.1907, found 460.1912; IR (neat): 3052, 1712, 1631, 1056 ($\nu_{B\text{-}F}$), 755 and 557 cm^{-1}.

2-Butyl-1,3,4-triphenylisoquinolin-2-ium tetrafluoroborate (**5ca**)



Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.87 (d, *J* = 7.6 Hz, 1 H), 7.82-7.80 (m, 2 H), 7.70-7.68 (m, 3 H), 7.65 (d, *J* = 7.2 Hz, 1 H), 7.60 (d, *J* = 8.4 Hz, 2 H), 7.56-7.54 (m, 2 H), 7.29-7.24 (m, 8 H), 4.37-4.33 (m, 2 H), 1.56 (q, *J* = 4.0 Hz, 2 H), 0.74-0.69 (m, 2 H), 0.36 (t, *J* = 7.4 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.3 (C), 144.7 (C), 139.7 (C), 138.2 (C), 135.9 (*C*H), 133.9 (C), 131.8 (C), 131.1 (*C*H), 130.9 (2 *C*H), 130.6 (*C*H), 130.5 (*C*H), 130.3 (2 *C*H), 129.6 (*C*H), 129.4 (2 *C*H), 129.2 (2 *C*H), 128.4 (C), 128.3 (2 *C*H), 128.2 (*C*H, C), 128.1 (2 *C*H), 126.7 (*C*H), 56.5 (*C*H_2), 31.9 (*C*H_2), 19.4 (*C*H_2), 12.4 (*C*H_3); **HRMS** (FAB$^+$) cal for $C_{31}H_{28}N$ 414.2216, found 414.2242; IR (neat): 3051, 1631, 1055 ($\nu_{B\text{-}F}$), 755 and 555 cm^{-1}.

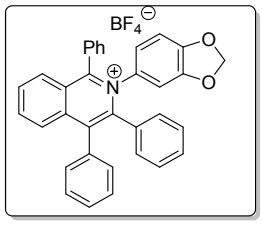
2-Benzyl-1,3,4-triphenylisoquinolin-2-ium tetrafluoroborate (**5da**)



Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.93 (t, *J* = 7.6 Hz, 1 H), 7.74-7.66 (m, 5 H), 7.58-7.51 (m, 3 H), 7.27-7.24 (m, 7 H), 7.18-7.05 (m, 6 H), 6.50 (d, *J* = 7.6 Hz, 2 H), 5.74 (s, 2 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 160.9 (C), 145.7 (C), 140.4 (C), 139.0 (C), 137.3 (*C*H), 134.6

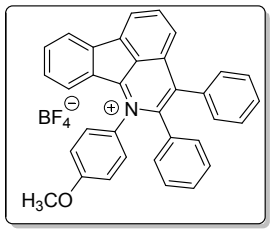
(C), 134.0 (C), 131.9 (C), 131.7 (*C*H), 131.4 (*C*H), 131.3 (*C*H), 130.9 (2 *C*H), 130.6 (2 *C*H), 129.9 (*C*H), 129.5 (2 *C*H), 129.4 (2 *C*H), 129.1 (2 *C*H), 128.8 (*C*H, C), 128.6 (2 *C*H), 128.5 (*C*H, C), 128.4 (2 *C*H), 127.2 (*C*H), 126.0 (2 *C*H), 60.4 (CH_2); EI mass cal for $C_{34}H_{26}N$ 448.2060, found 448.2; IR (neat): 2939, 1666, 1612 cm^{-1}.

2-(Benzo[*d*][1,3]dioxol-5-yl)-1,3,4-triphenylisoquinolin-2-ium tetrafluoroborate (5ea)



Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06-8.03 (m, 1 H), 7.85-7.84 (m, 2 H), 7.79 (d, *J* = 8.4 Hz, 1 H), 7.53-7.31 (m, 10 H), 7.23-7.17 (m, 2 H), 7.07-7.02 (m, 3 H), 6.82 (sd, *J* = 1.6 Hz, 1 H), 6.78 (d, *J* = 8.4 Hz, 1 H), 6.44 (d, *J* = 8.4 Hz, 1 H), 5.81 (d, *J* = 5.2 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.2 (C), 148.5 (C), 148.0 (C), 146.0 (C), 140.0 (C), 139.5 (C), 134.2 (C), 134.1 (C), 132.5 (C), 131.8 (*C*H), 131.7 (*C*H), 131.6 (2 CH), 131.3 (2 *C*H), 130.9 (C), 130.9 (*C*H), 130.8 (*C*H), 130.7 (*C*H), 130.6 (*C*H), 130.5 (*C*H), 129.1 (*C*H), 128.8 (2 *C*H), 128.7 (*C*H), 128.6 (*C*H), 128.3 (C), 128.0 (*C*H), 127.9 (*C*H), 127.3 (*C*H), 123.3 (*C*H), 109.8 (*C*H), 107.6 (*C*H), 102.7 (CH_2); **HRMS** (FAB^+) cal for $C_{34}H_{24}NO_2$ 478.1802, found 478.1781; IR (neat): 3051, 1631, 1056 ($\nu_{B\text{-}F}$), 755 and 557 cm^{-1}.

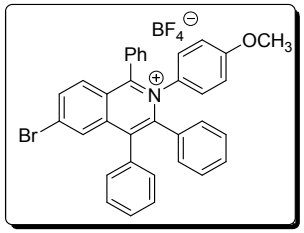
1-(4-Methoxyphenyl)-2,3-diphenylindeno[1,2,3-ij]isoquinolin-1-iumtetrafluoroborate (5fa)

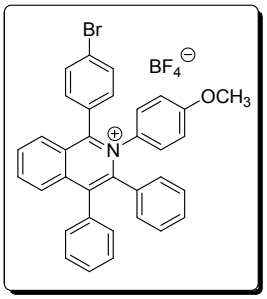


Brown solid; **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.94 (d, *J* = 6.8 Hz, 1 H), 7.83 (t, *J* = 7.6 Hz, 1 H), 7.76 (d, *J* = 7.2 Hz, 1 H), 7.50-7.39 (m, 4 H), 7.33-7.32 (m, 2 H), 7.28-7.22 (m, 6 H), 7.05-7.00 (m, 3 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 6.05 (d, *J* = 7.6 Hz, 1 H), 3.81 (s, 3 H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 161.2 (C), 155.9 (C), 148.7 (C), 141.8 (C), 139.3 (*C*H), 138.8 (C), 138.0 (C), 136.4 (C), 134.7 (*C*H), 133.2 (C), 132.0 (2 *C*H), 131.9 (C), 131.5 (C), 131.2 (2 *C*H), 131.0 (C), 129.9 (*C*H), 129.3 (*C*H), 128.7 (*C*H), 128.6 (2 *C*H), 128.3 (2 *C*H), 128.0 (2 *C*H), 127.8 (C), 127.2 (*C*H), 127.0 (*C*H), 125.8 (*C*H), 124.0 (*C*H), 115.3 (2 *C*H), 55.9 (O*C*H_3); **HRMS** (FAB$^+$) cal for $C_{34}H_{24}NO$ 462.1852, found 462.1842; IR (neat): 3051, 1630, 1055 ($\nu_{B\text{-}F}$), 755 and 557 cm^{-1}.

5-Methoxyphenanthridin-6(5*H*)-onetetrafluoroborate (5ba)



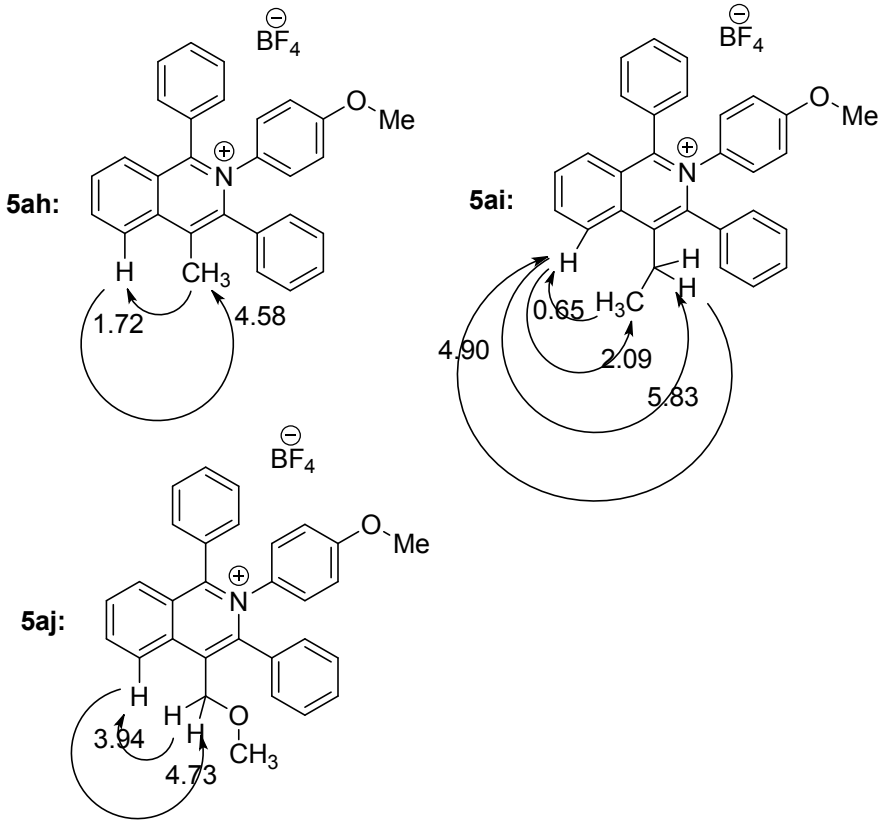


Brown solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (t, *J* = 7.4 Hz, 1 H), 7.94 (s, 1 H), 7.91 (d, *J* = 9.2 Hz, 1 H), 7.87-7.84 (m, 2 H), 7.81 (d, *J* = 8.8 Hz, 1 H), 7.71 (d, *J* = 8.8 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 2 H), 7.50-7.33 (m, 18 H), 7.20-7.12 (m, 8 H), 7.03 (m, 7 H), 6.56 (d, *J* = 8.4 Hz, 2 H), 6.52 (t, *J* = 7.6 Hz, 2 H), 3.61 (s, 3 H), 3.58 (s, 3 H);

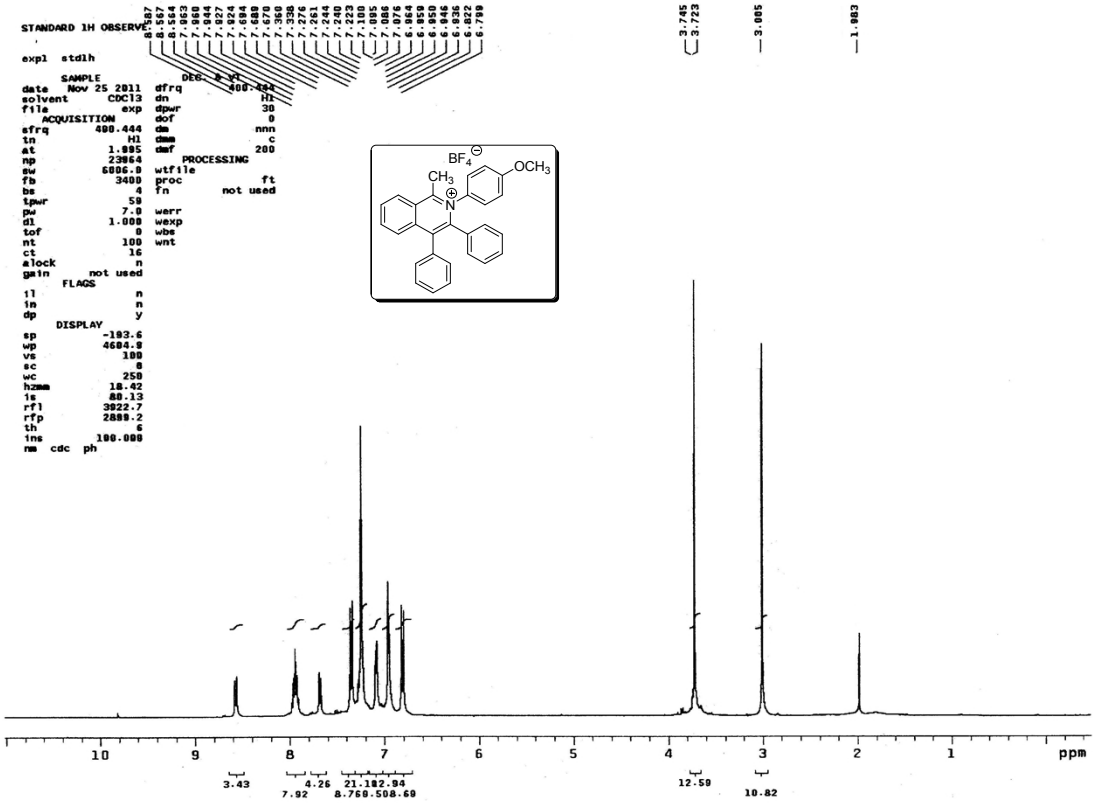
References:

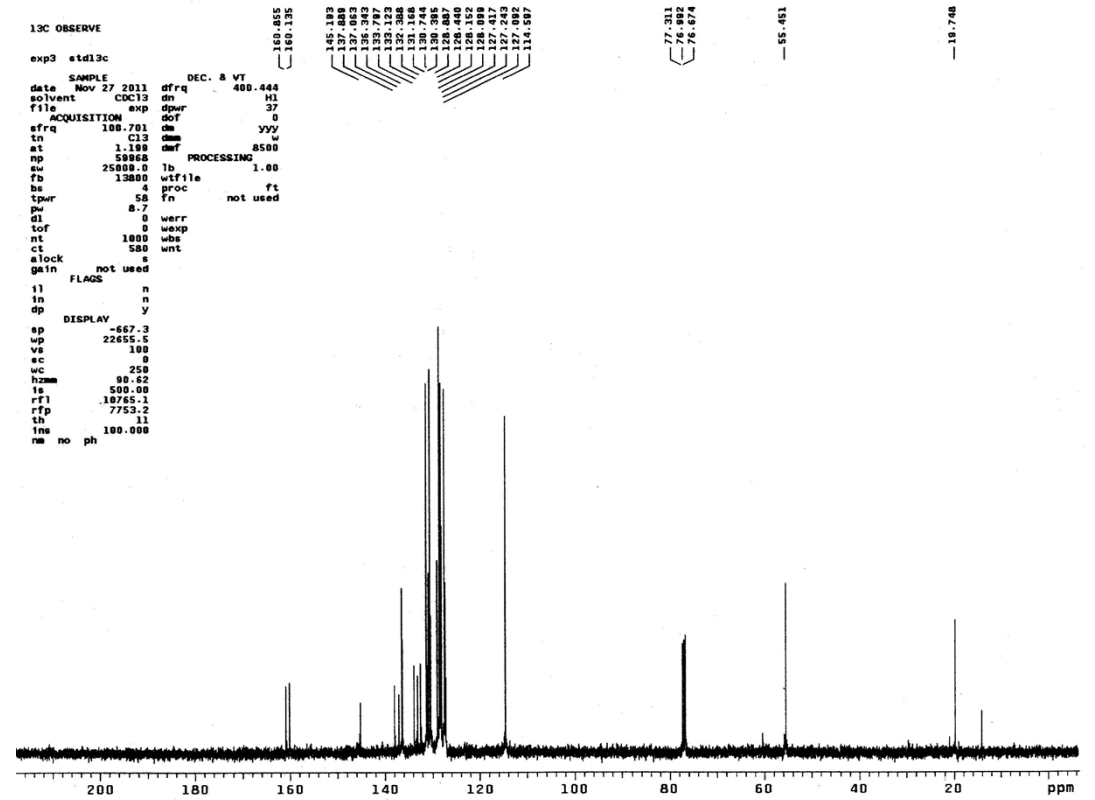
1. D. D. Perrin, W. L. F. Armarego, *In Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, **1988**.
2. W. Li, G. Hou, M. Chang, X. Chang, *Adv. Synth. Cat*., **2009**, *351*, 3123-3127.

NOE Experiments of 5ah, 5ai and 5aj

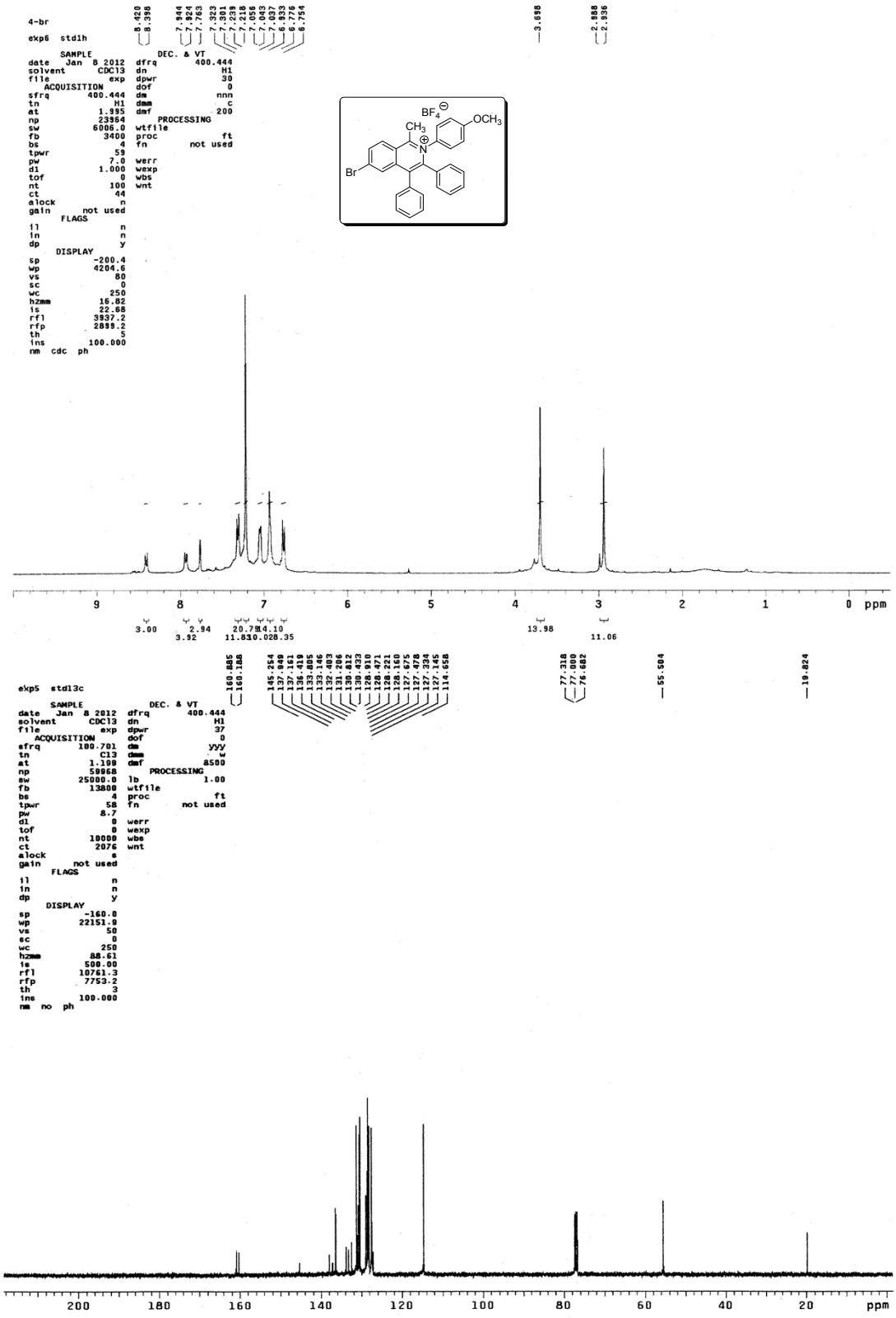


^{1}H and ^{13}C NMR spectra of compound **3aa**.

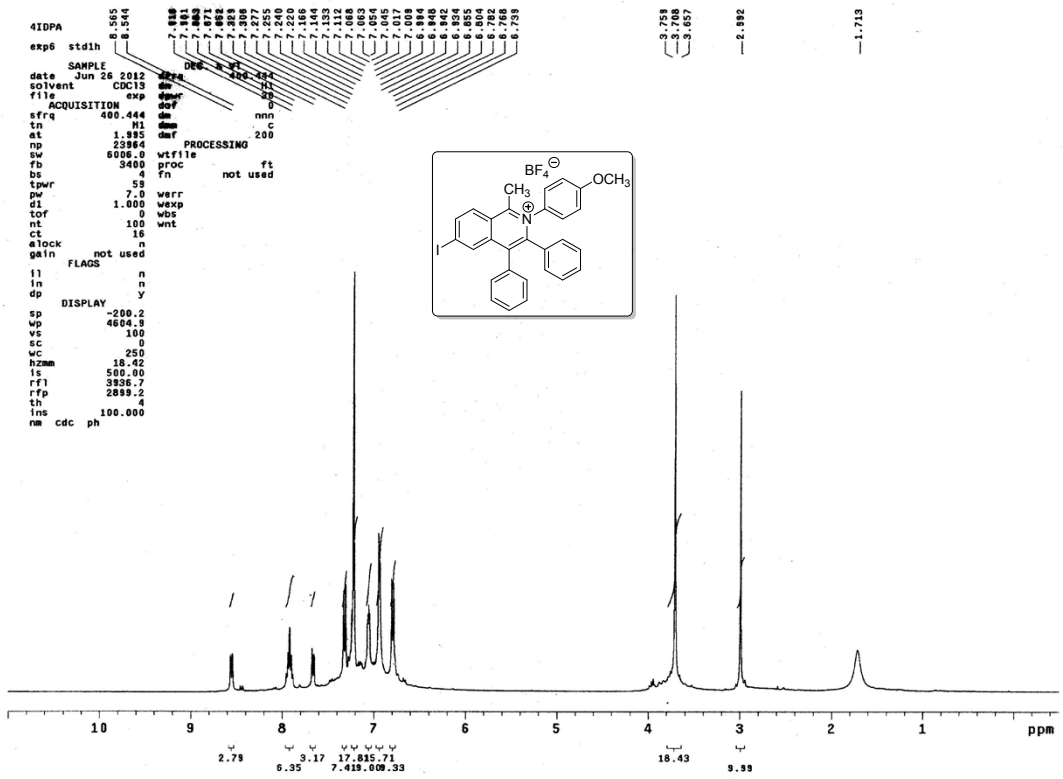


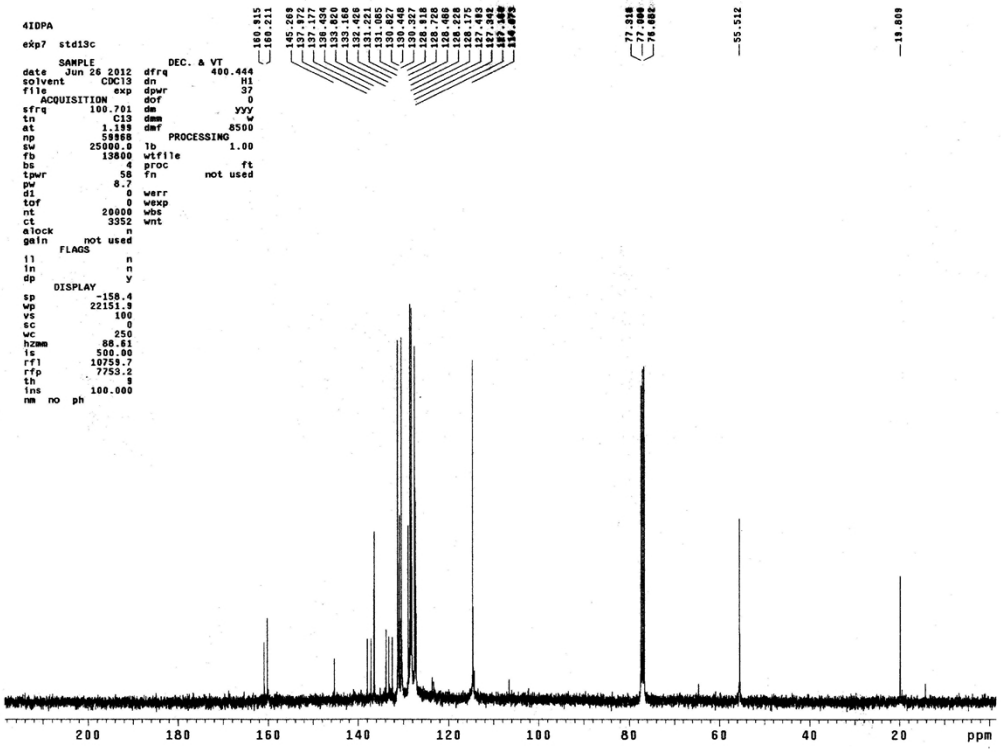


^{1}H and ^{13}C NMR spectra of compound **3ba**.

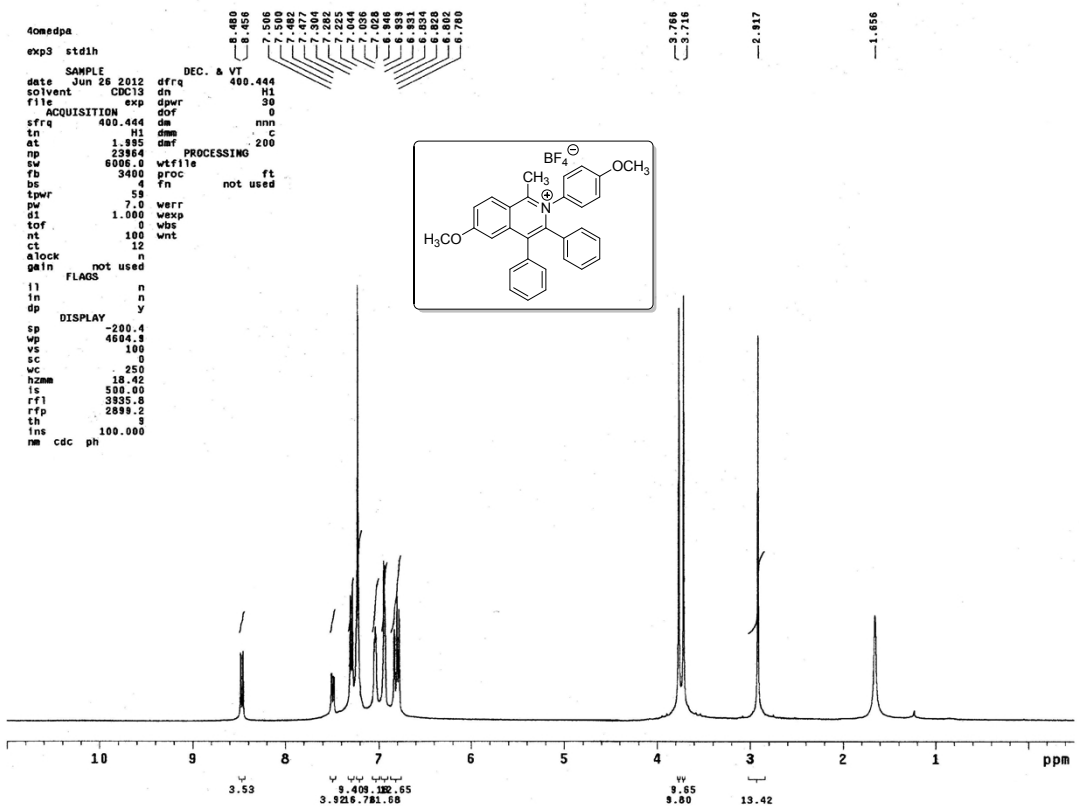


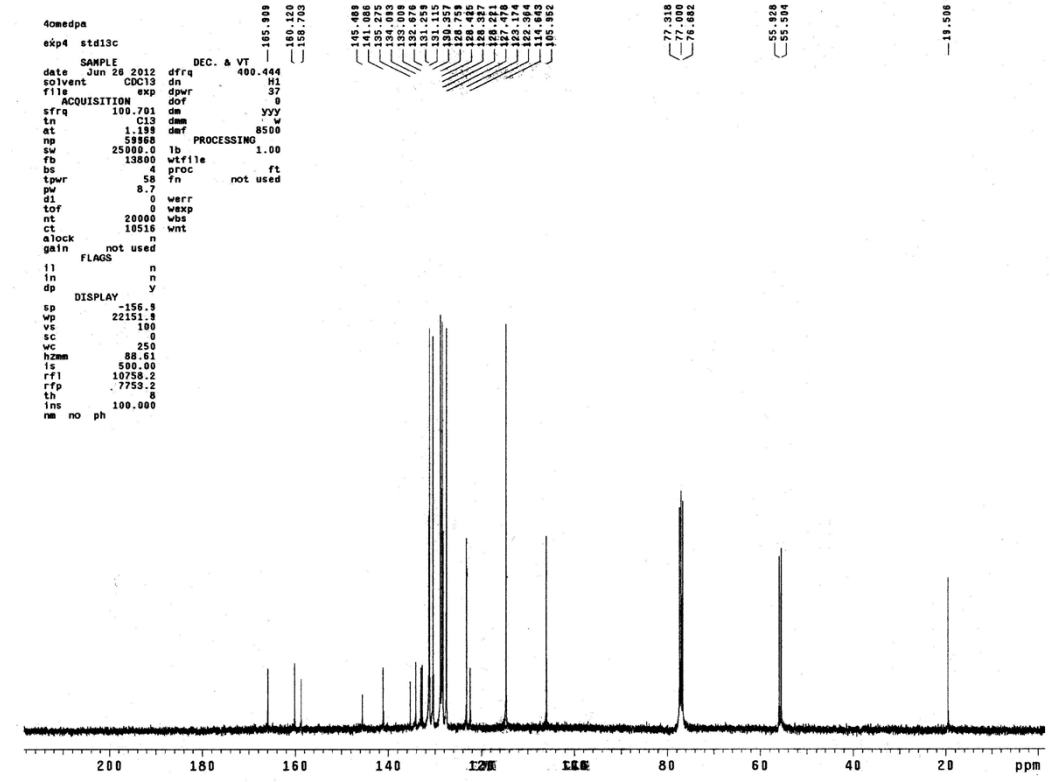
^{1}H and ^{13}C NMR spectra of compound **3ca**.



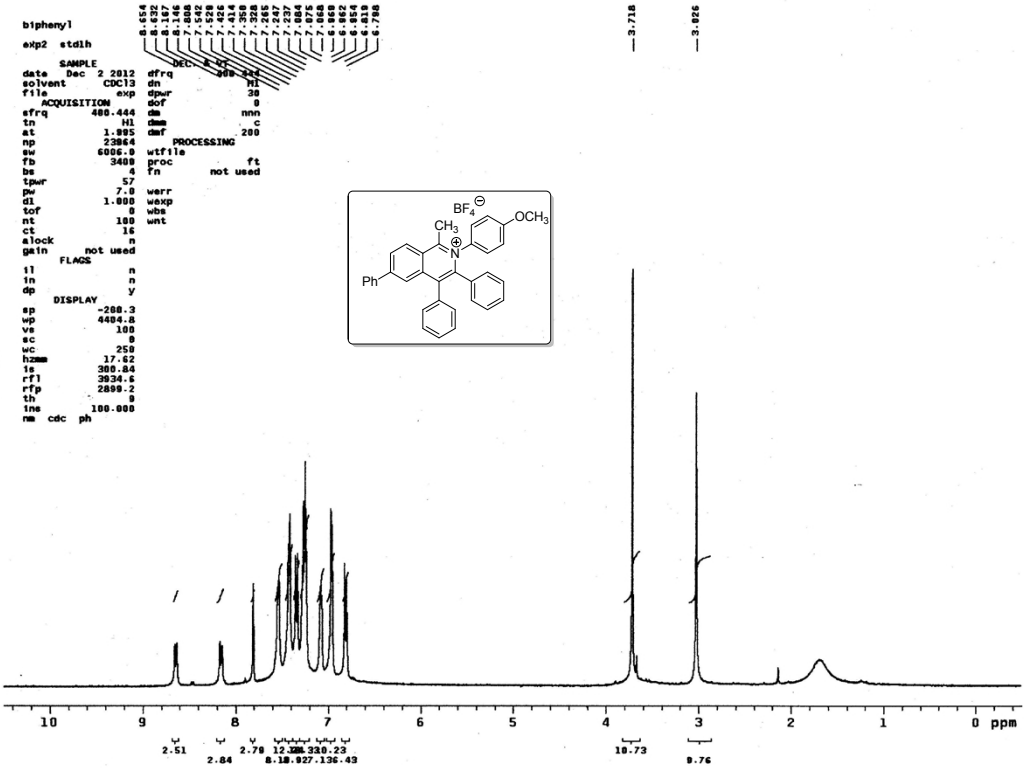


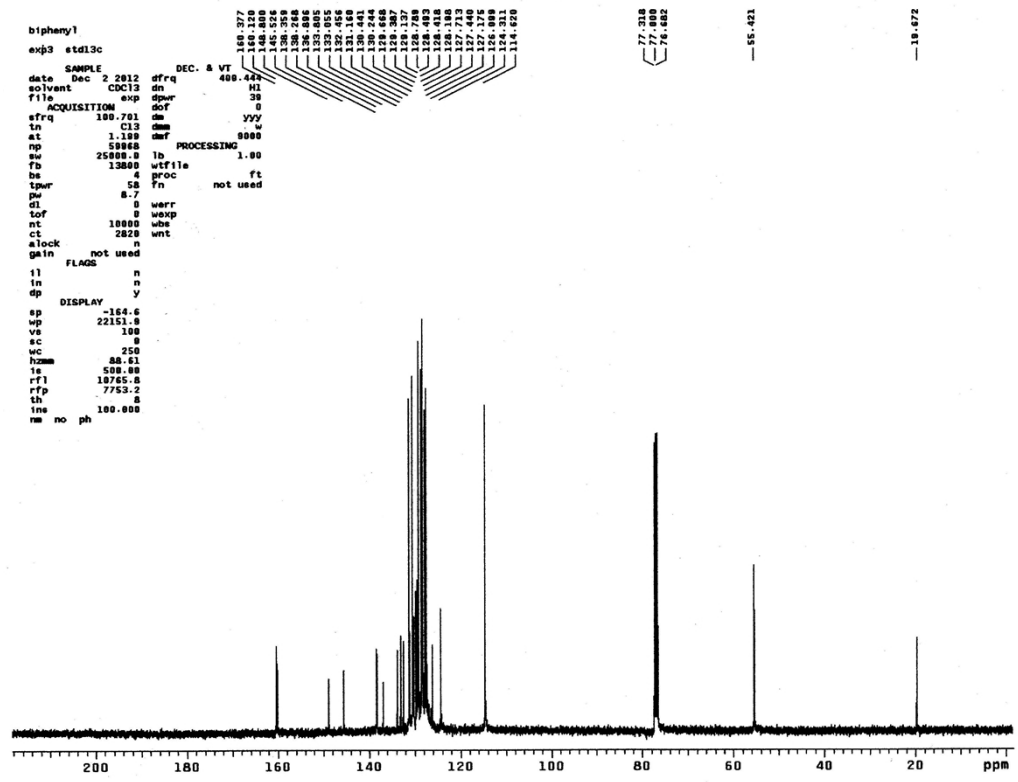
^{1}H and ^{13}C NMR spectra of compound **3da**.



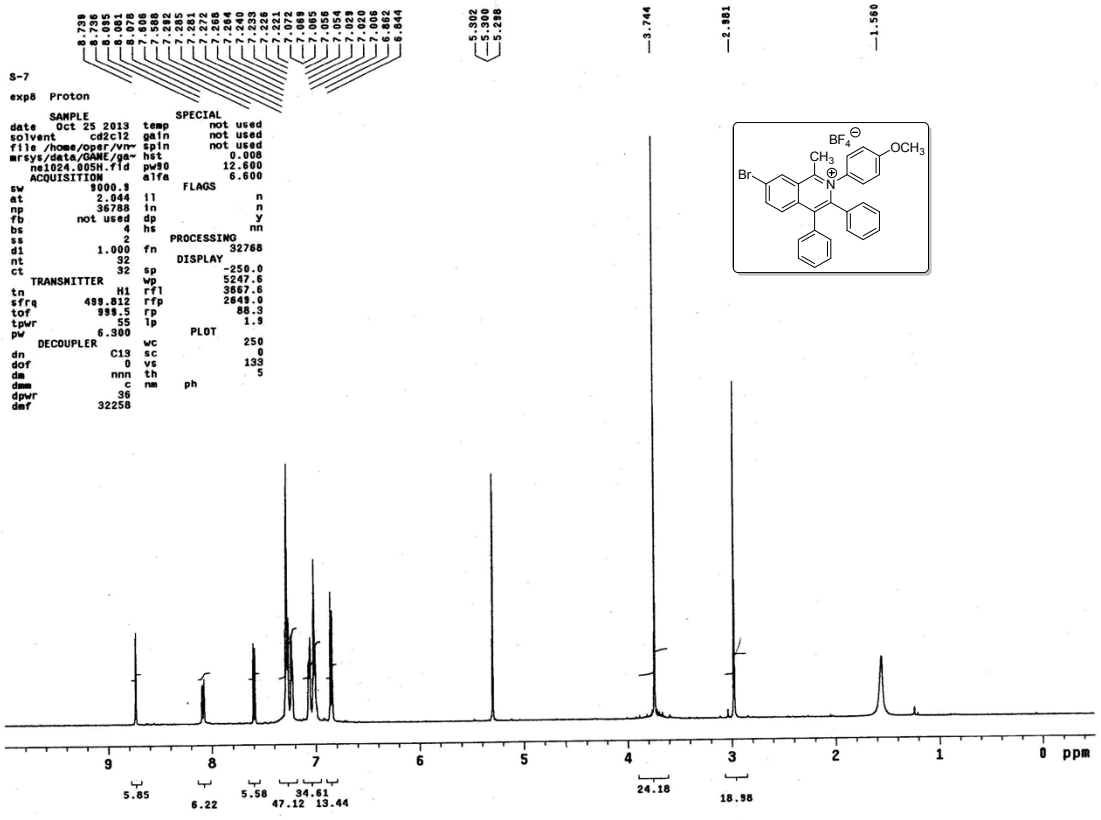


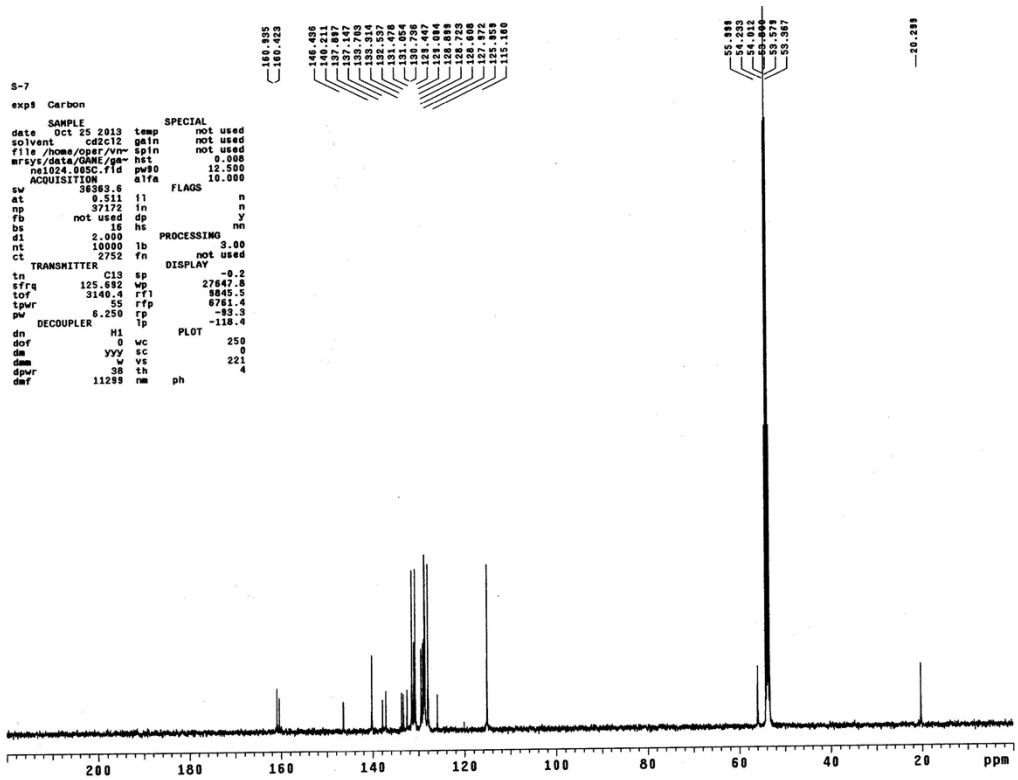
^{1}H and ^{13}C NMR spectra of compound **3ea**.



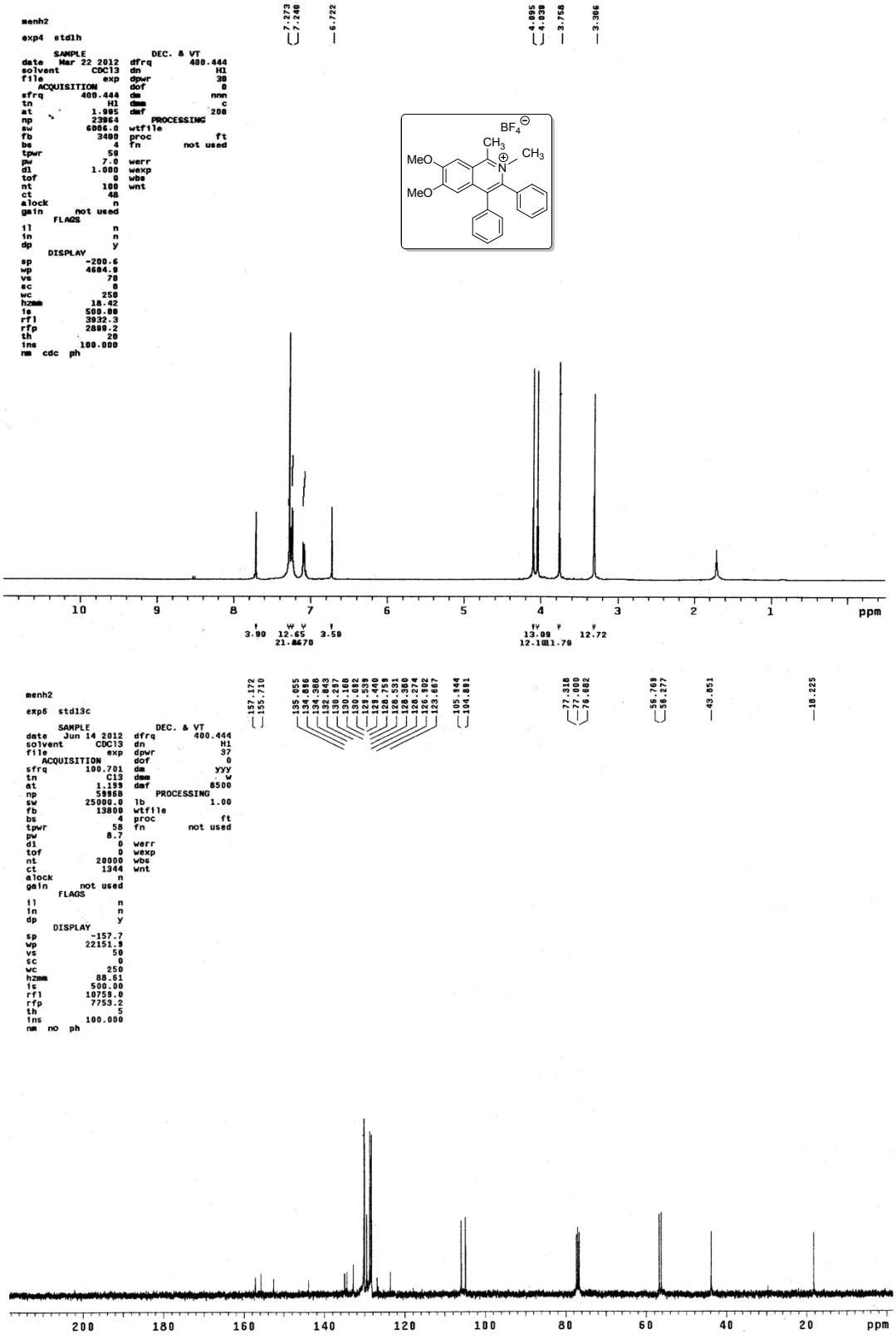


^{1}H and ^{13}C NMR spectra of compound **3fa**.

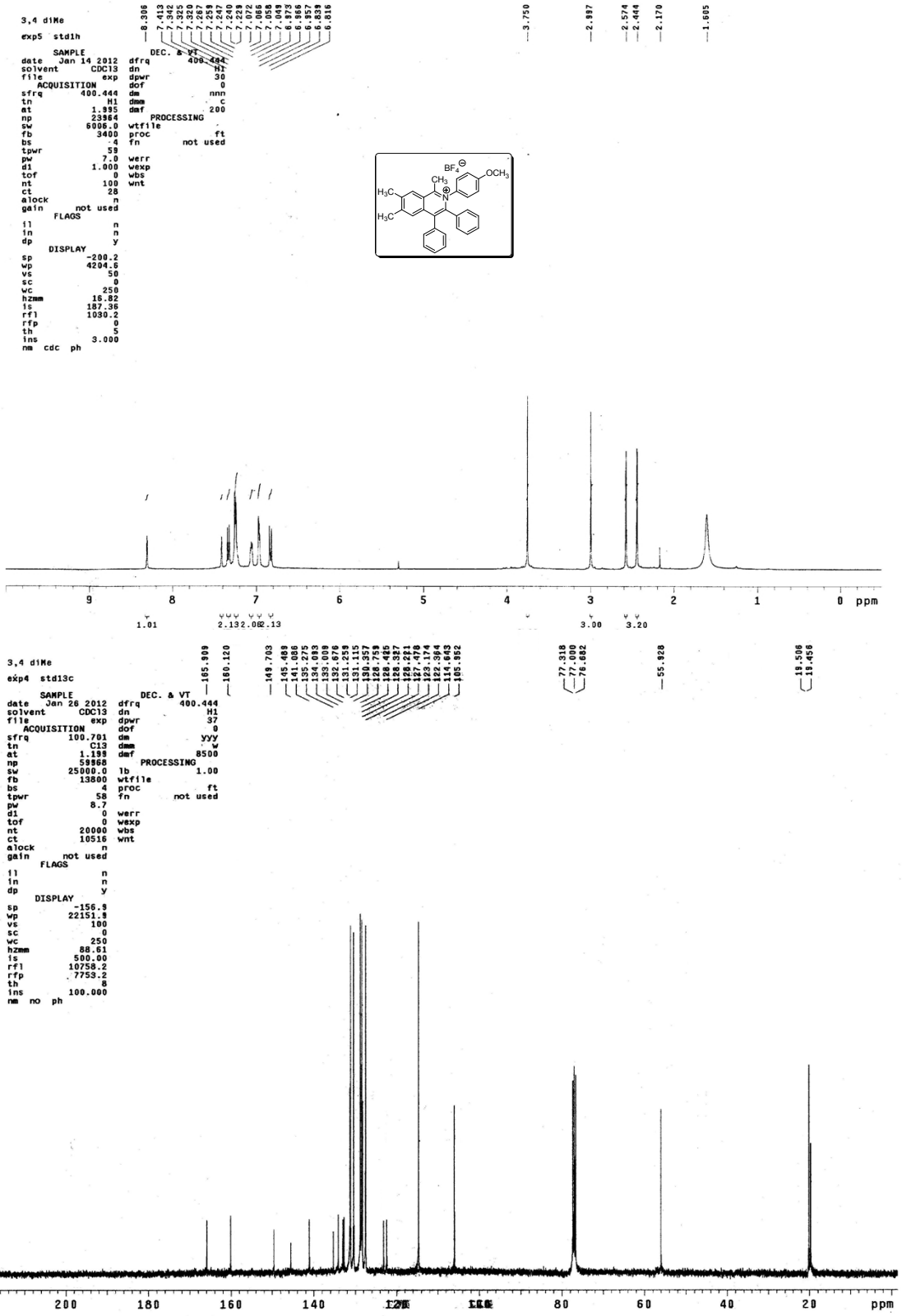




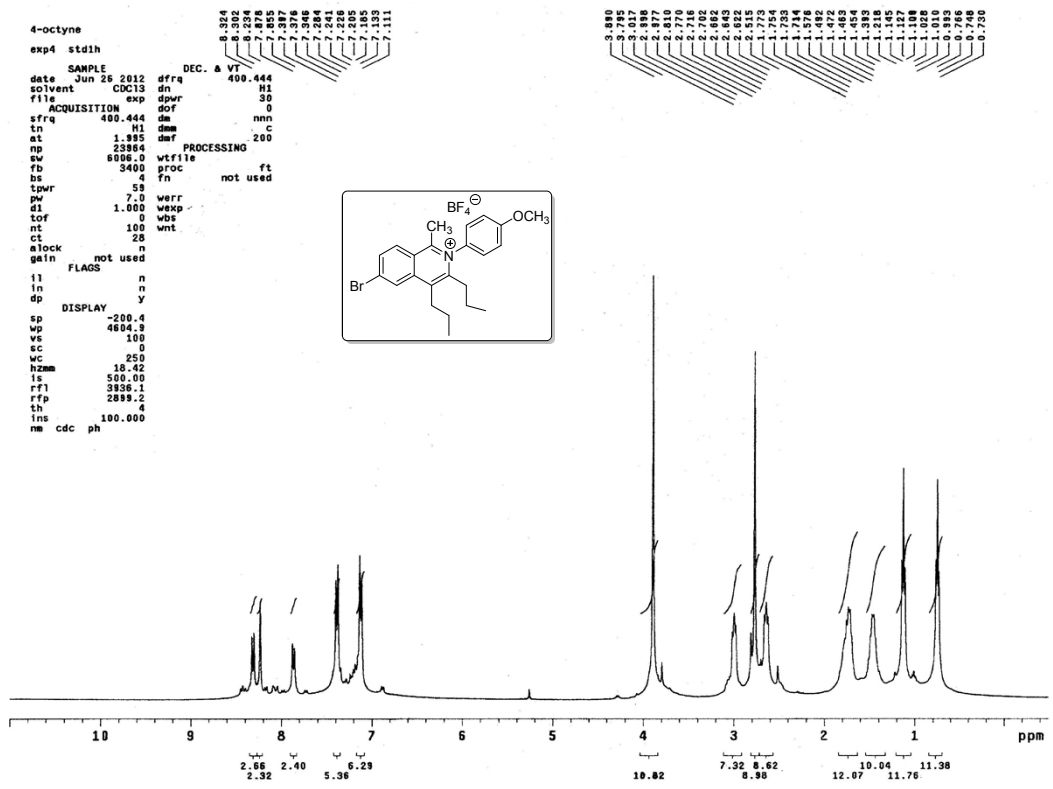
^{1}H and ^{13}C NMR spectra of compound **3ga**.

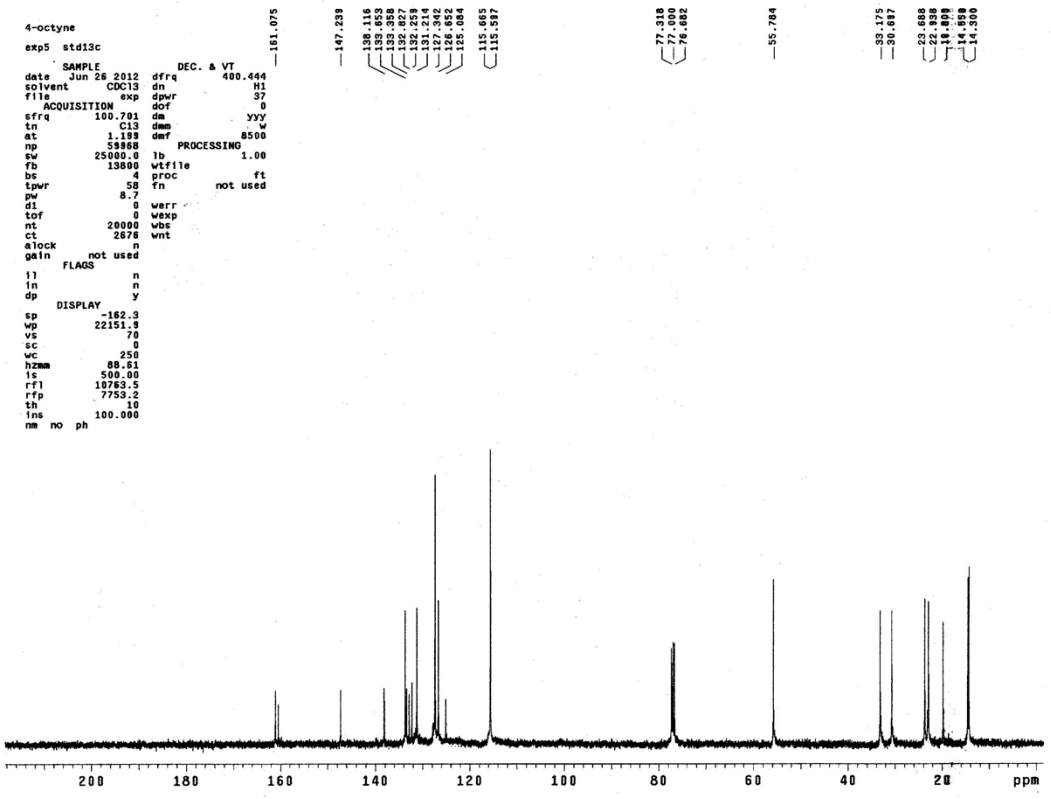


^{1}H and ^{13}C NMR spectra of compound **3ha**.

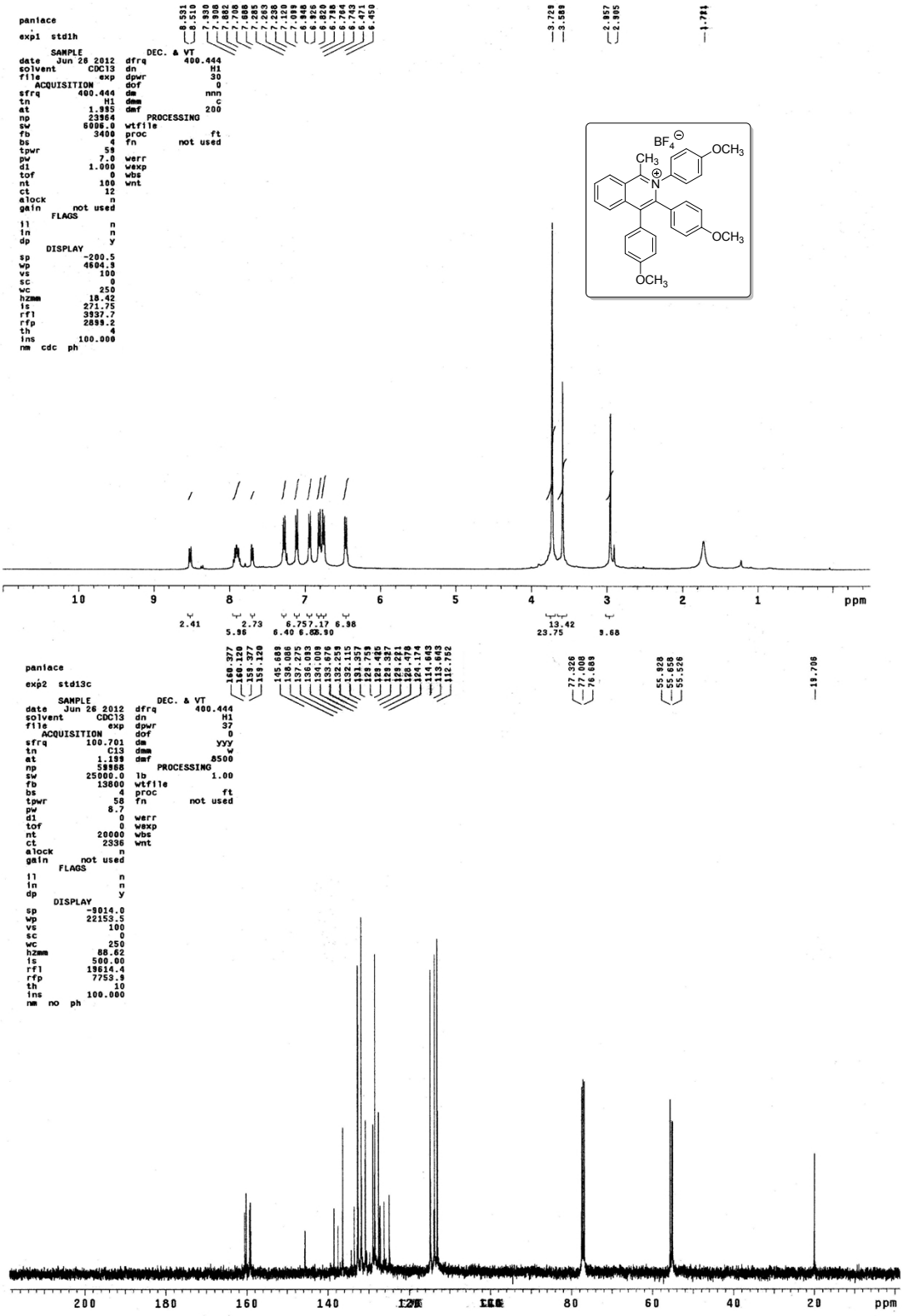


^{1}H and ^{13}C NMR spectra of compound **3bb**.

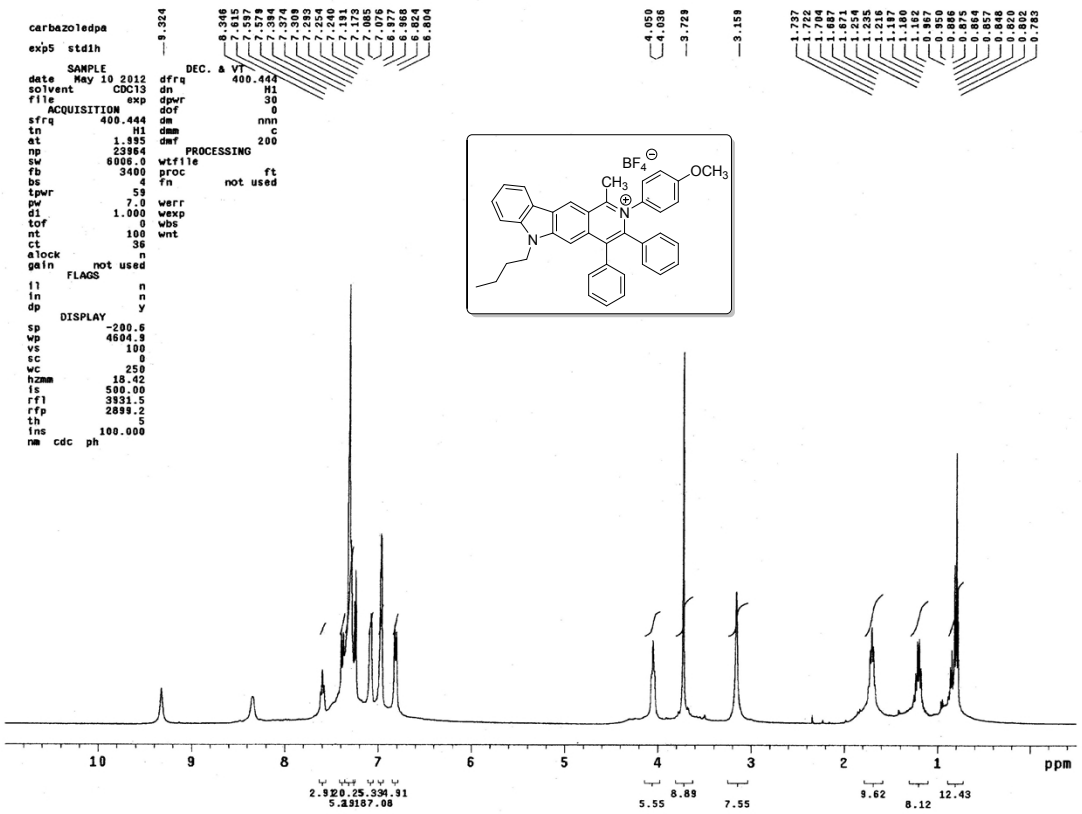


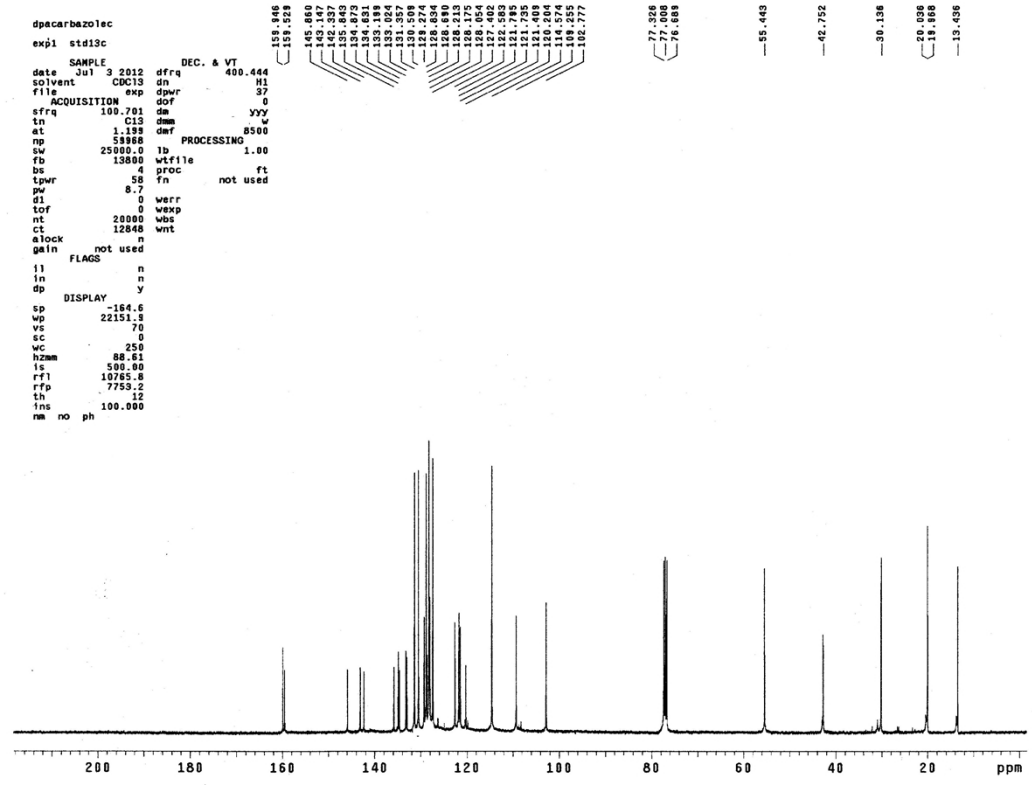


^{1}H and ^{13}C NMR spectra of compound **3ac**.

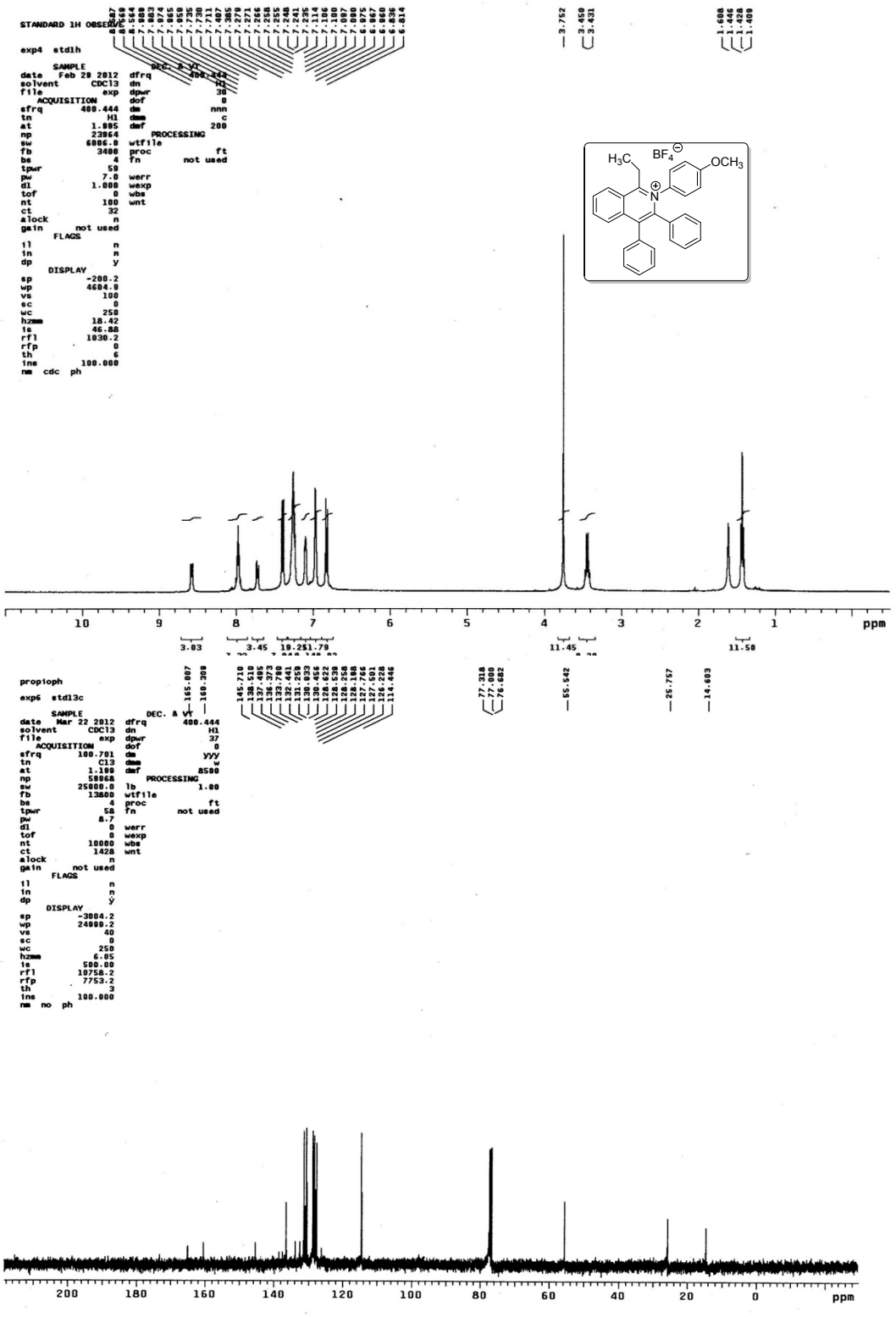


^{1}H and ^{13}C NMR spectra of compound **3ia**.

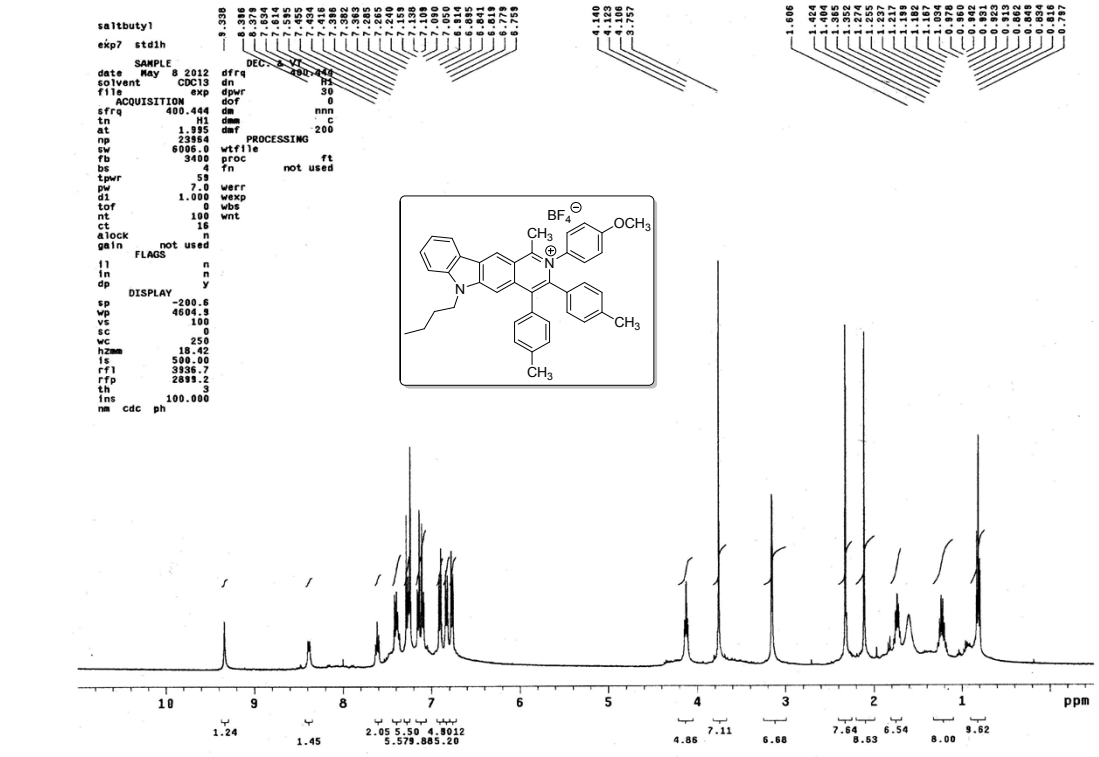


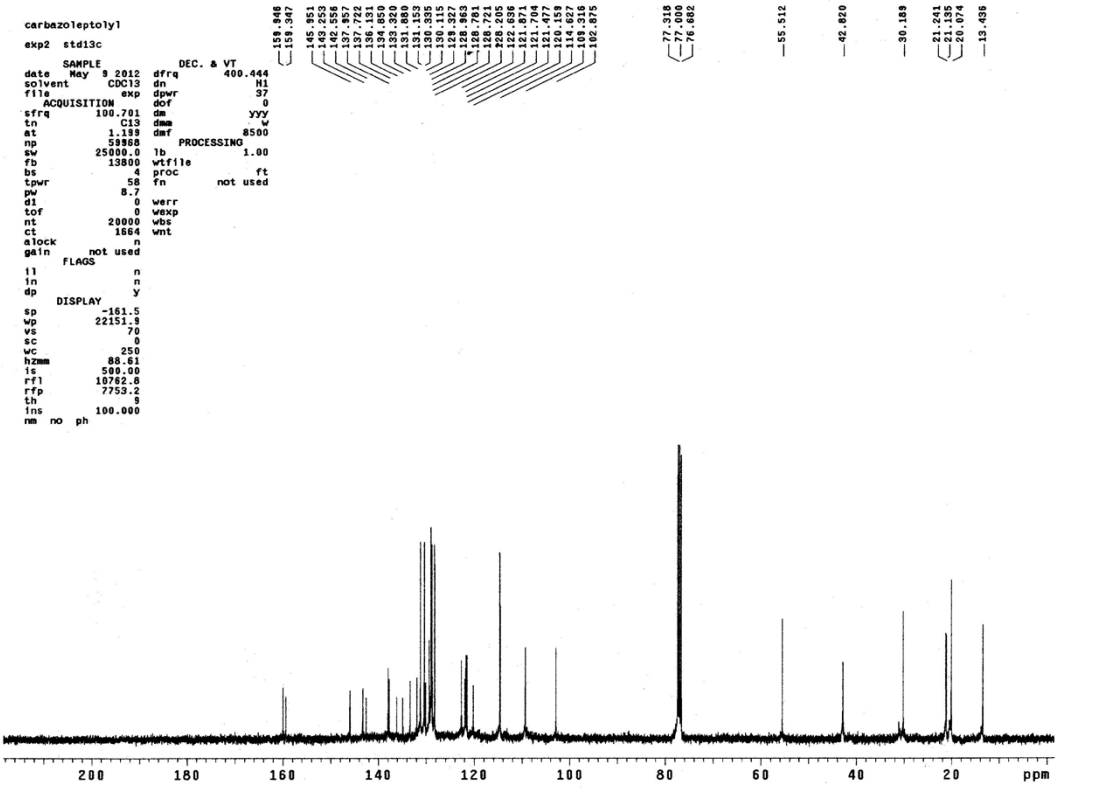


^{1}H and ^{13}C NMR spectra of compound **3ka**.

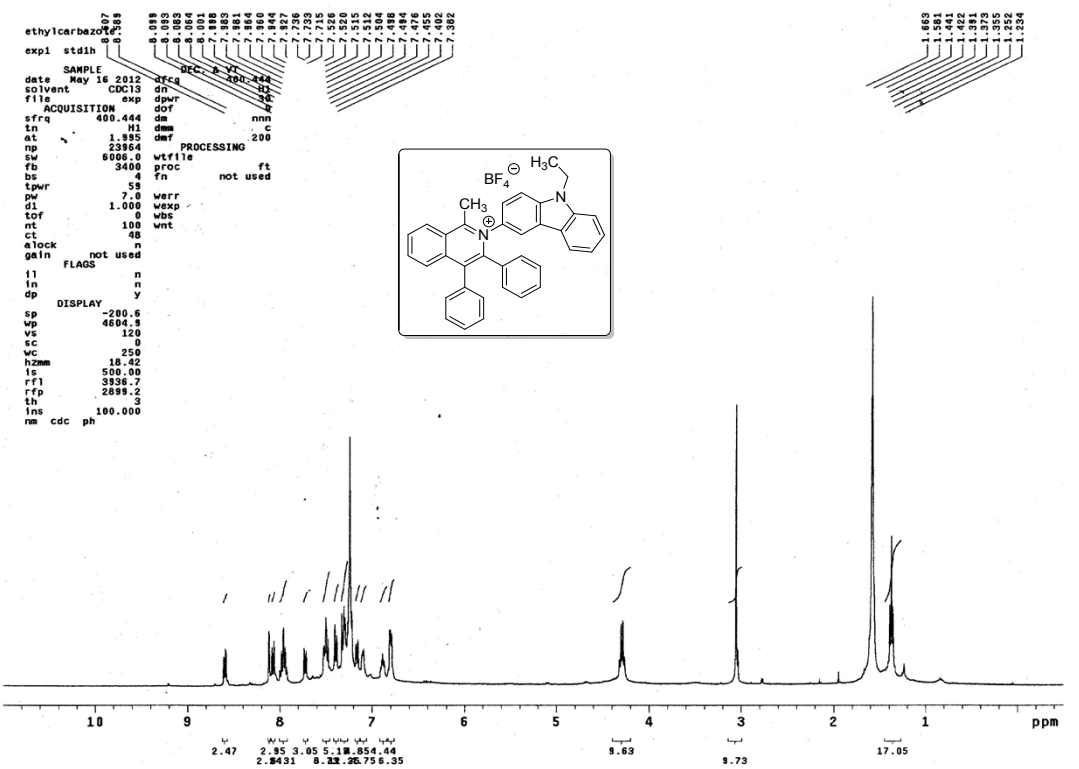


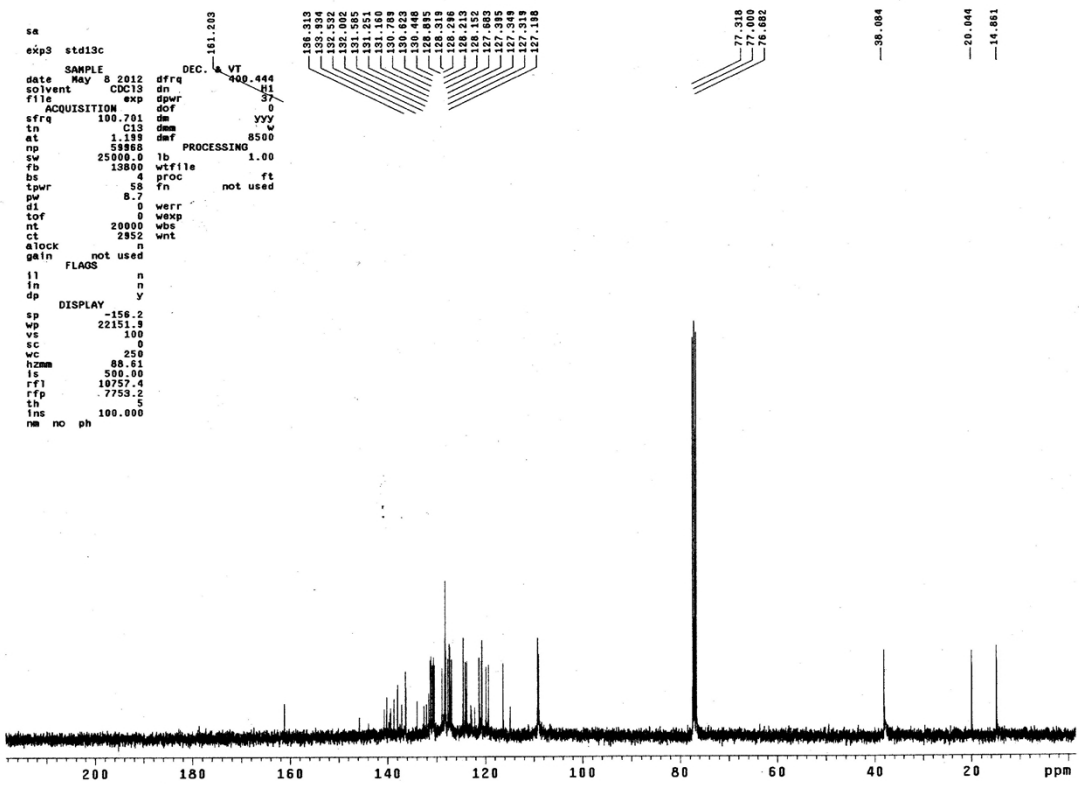
^{1}H and ^{13}C NMR spectra of compound **3ic**.



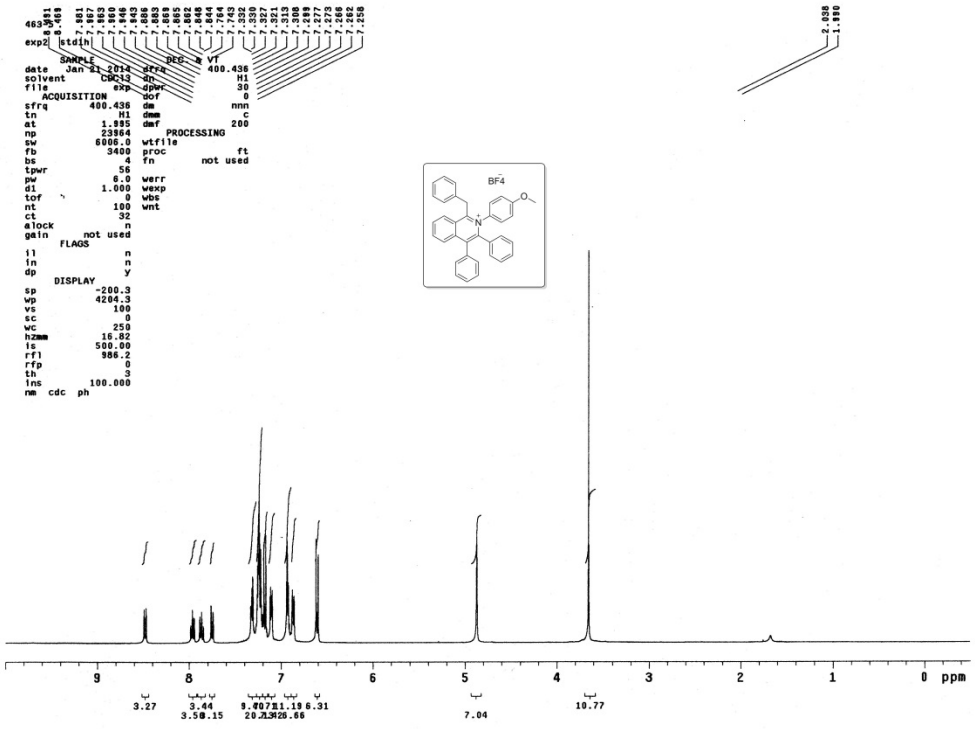


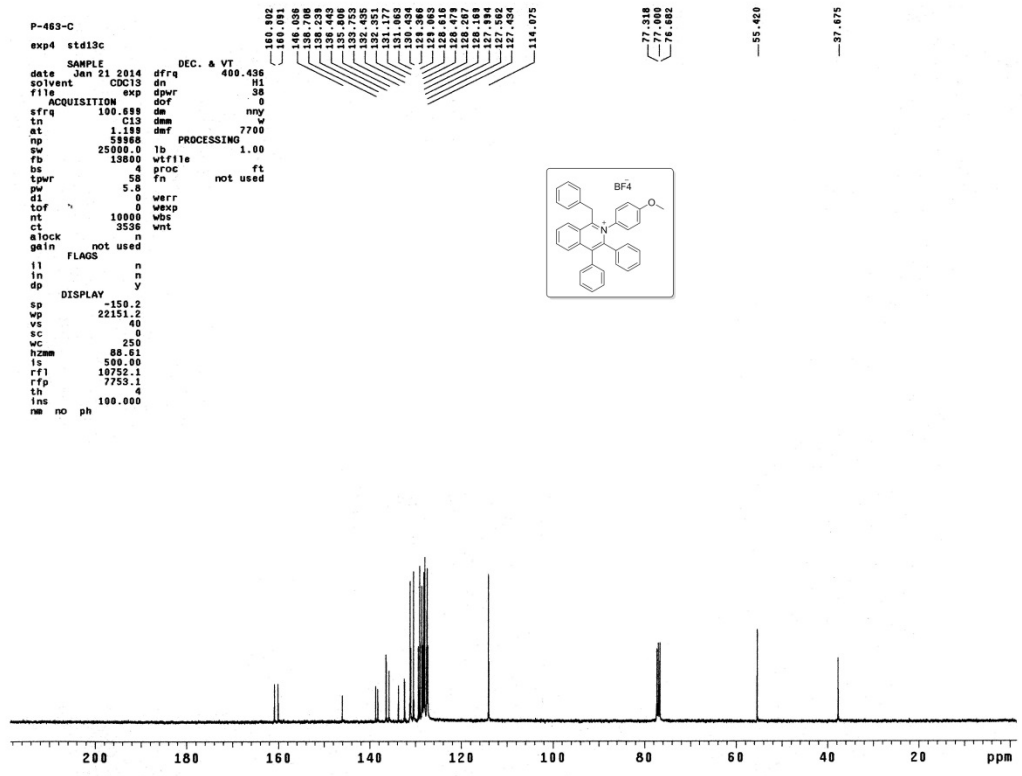
H and ^{13}C NMR spectra of compound **3ja**.



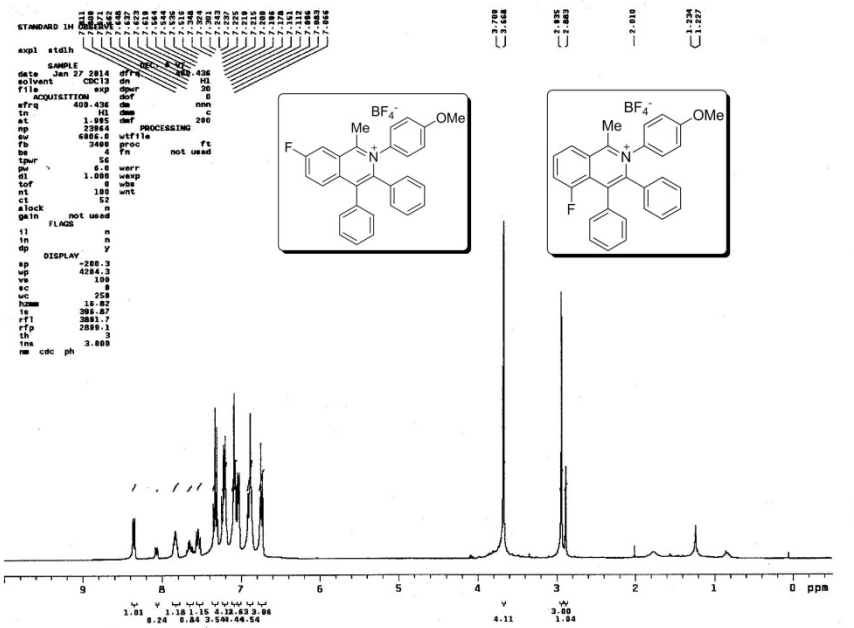


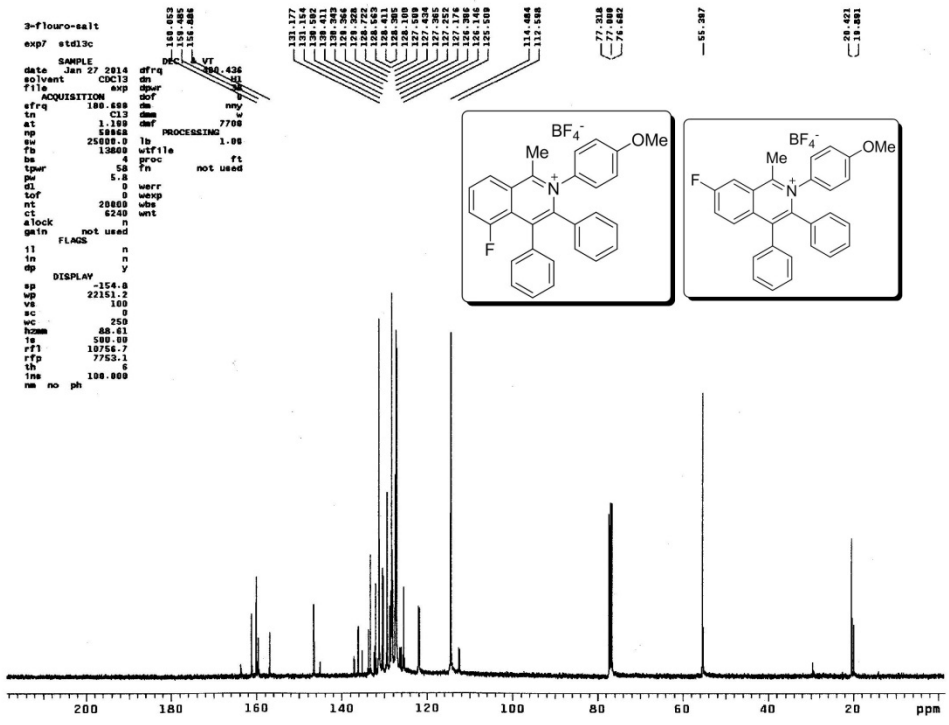
^{1}H and ^{13}C NMR spectra of compound **3la**



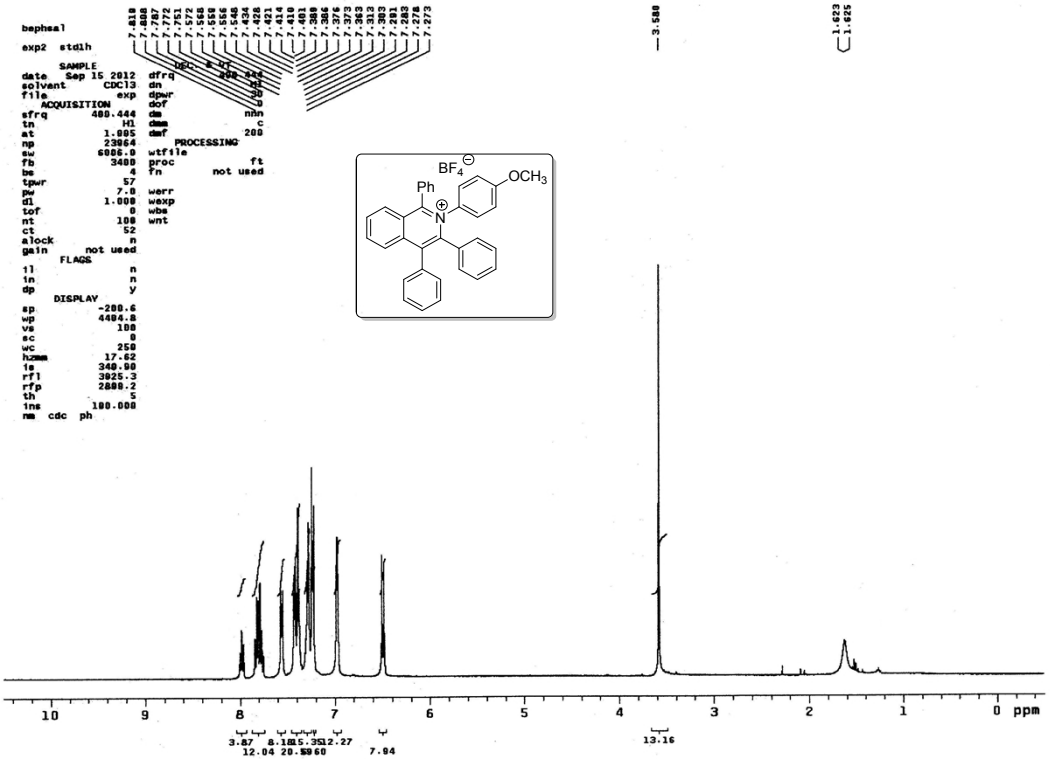


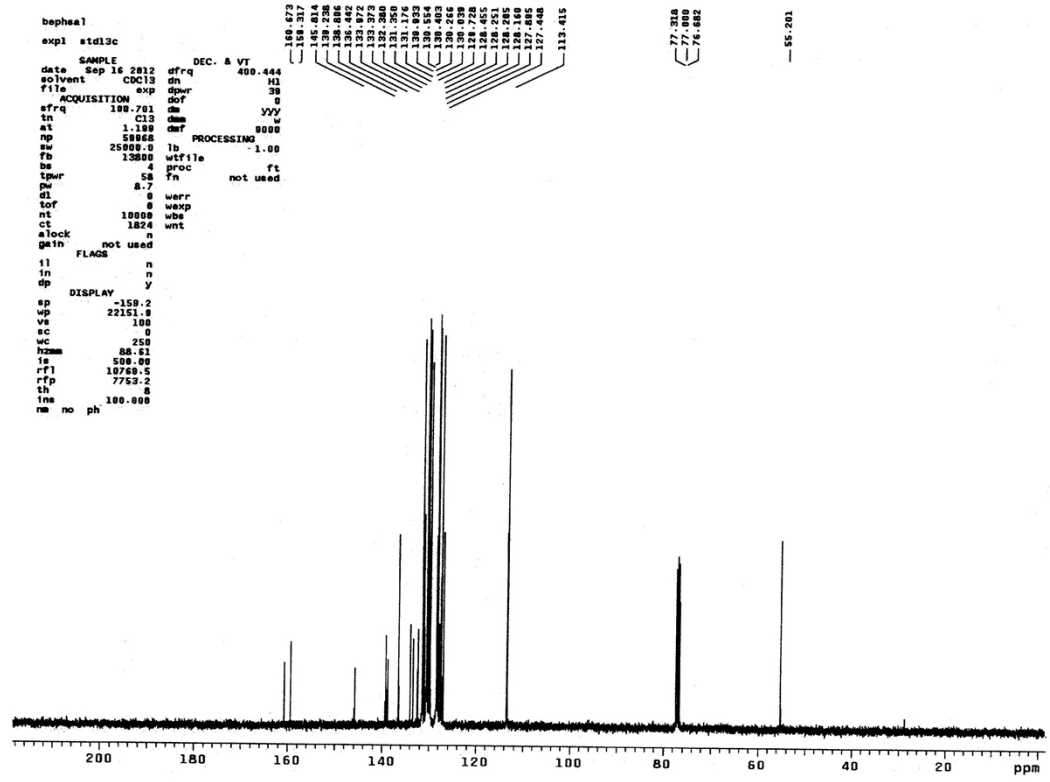
^{1}H and ^{13}C NMR spectra of compound **3ma** + **3ma'**



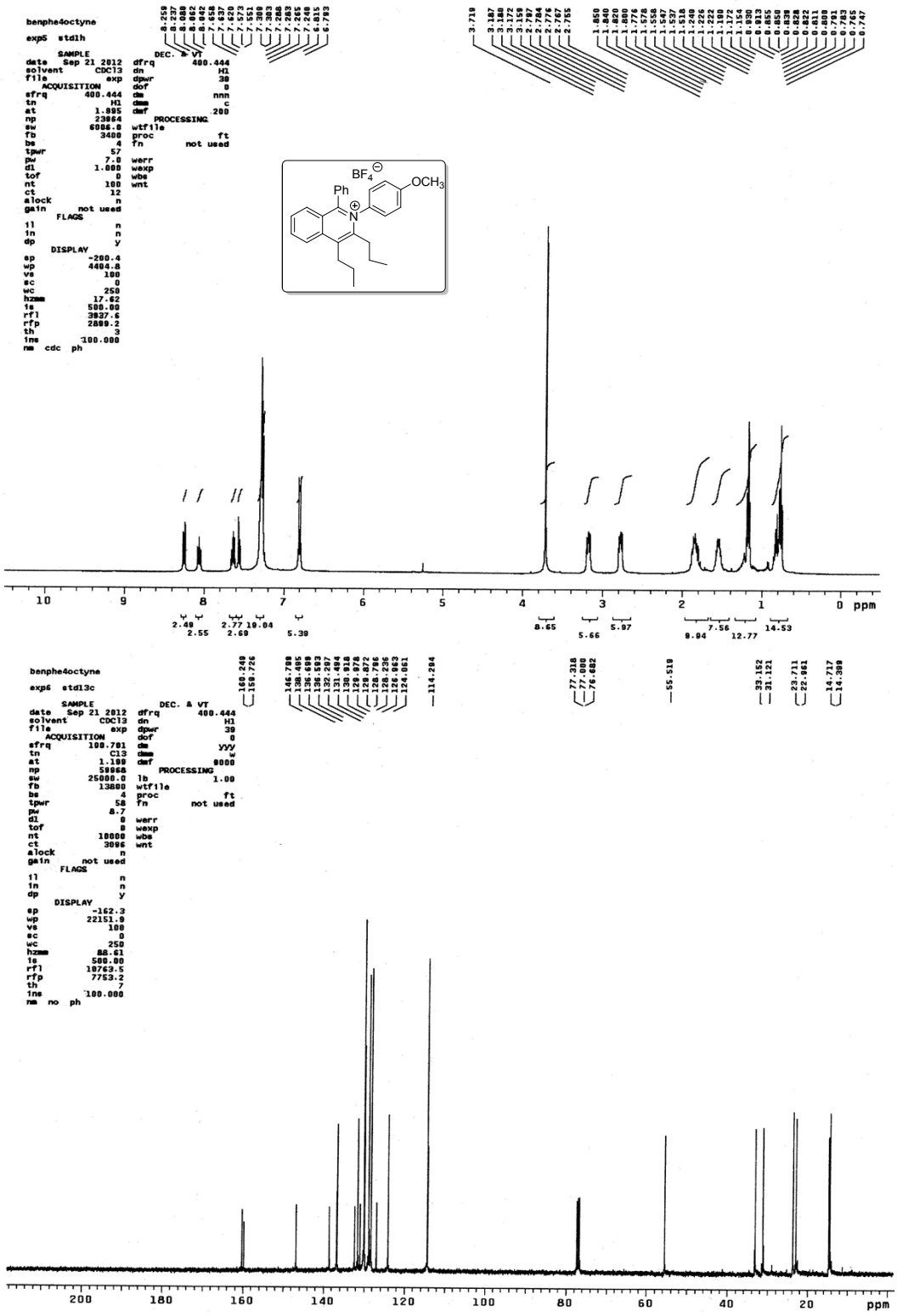


^{1}H and ^{13}C NMR spectra of compound **5aa**.

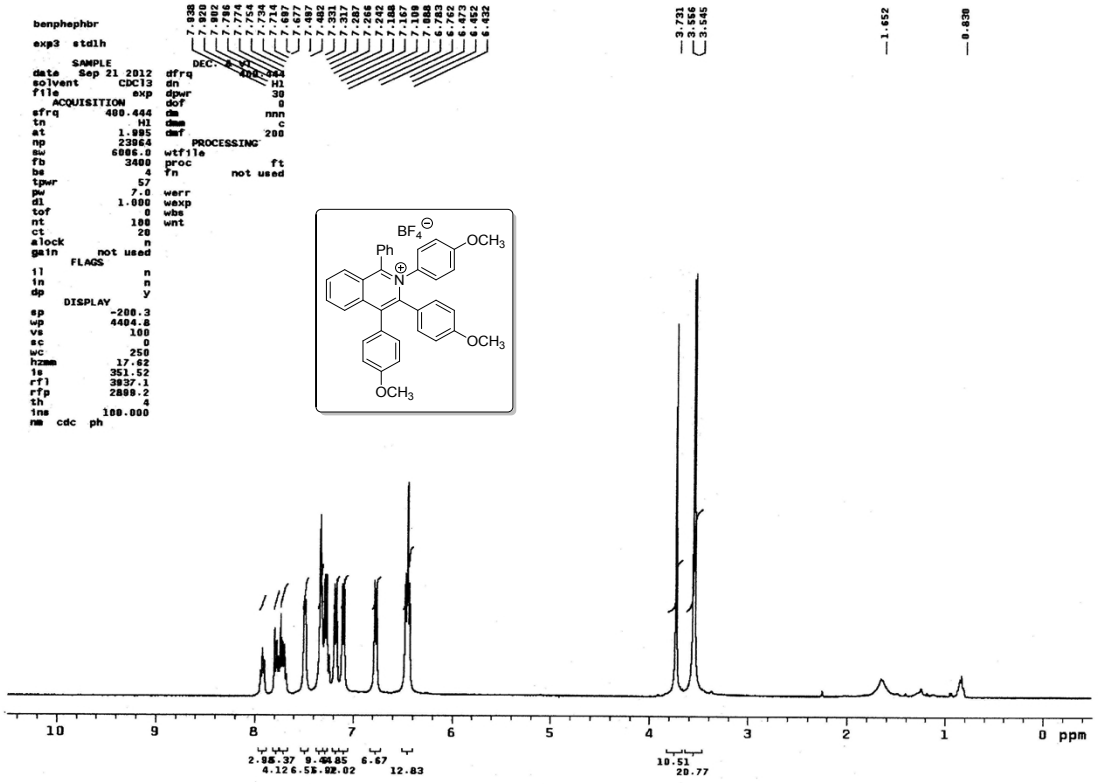


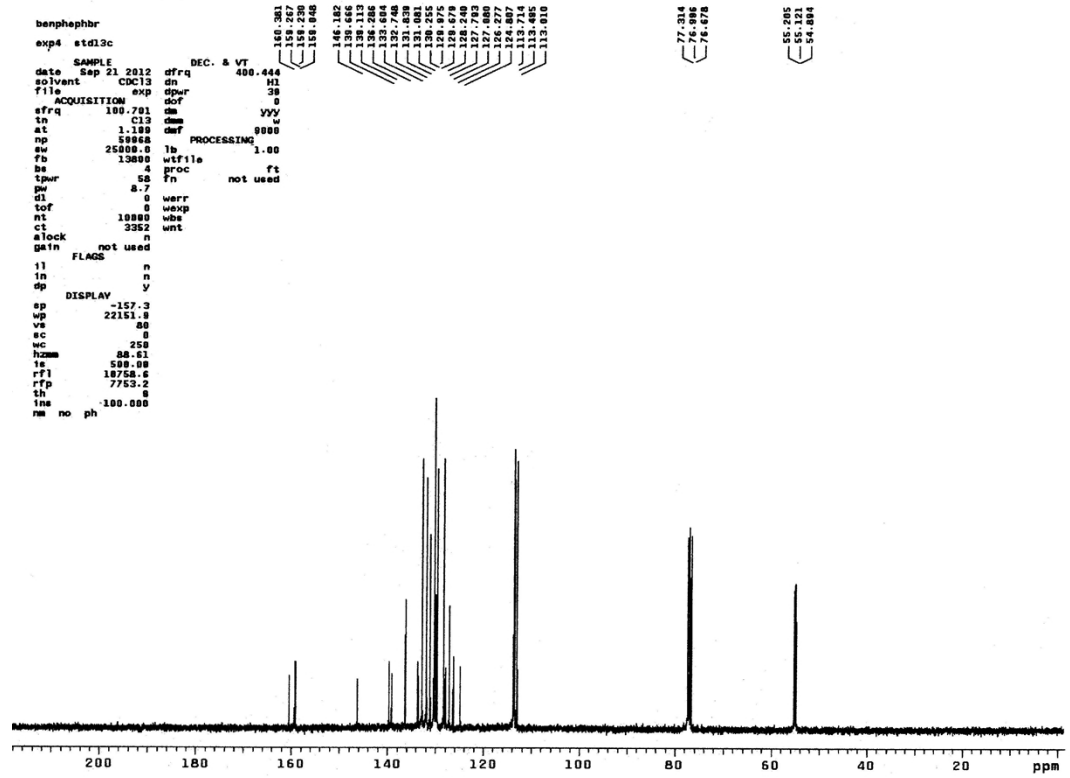


^{1}H and ^{13}C NMR spectra of compound **5ab**.

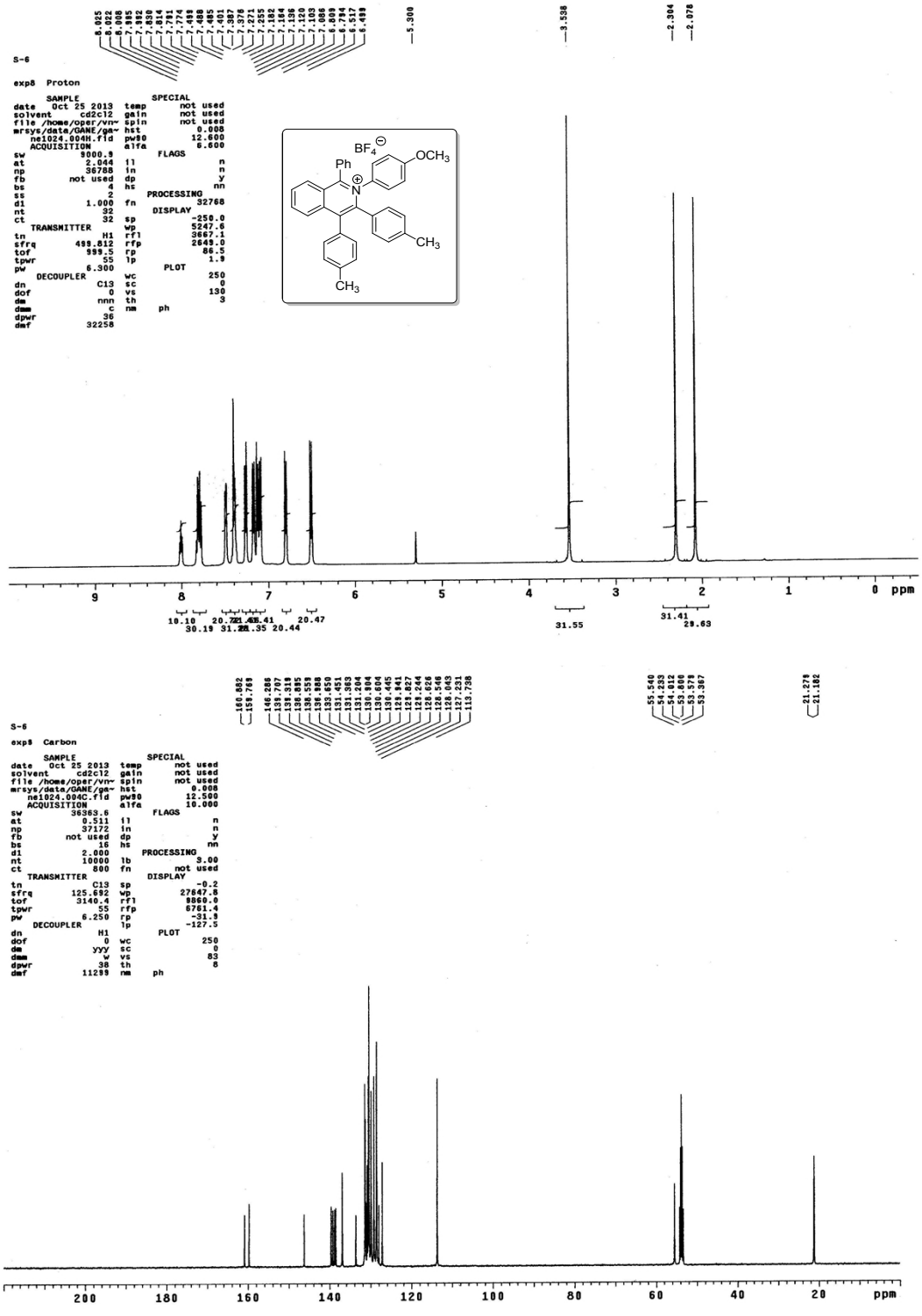


^{1}H and ^{13}C NMR spectra of compound **5ac**.

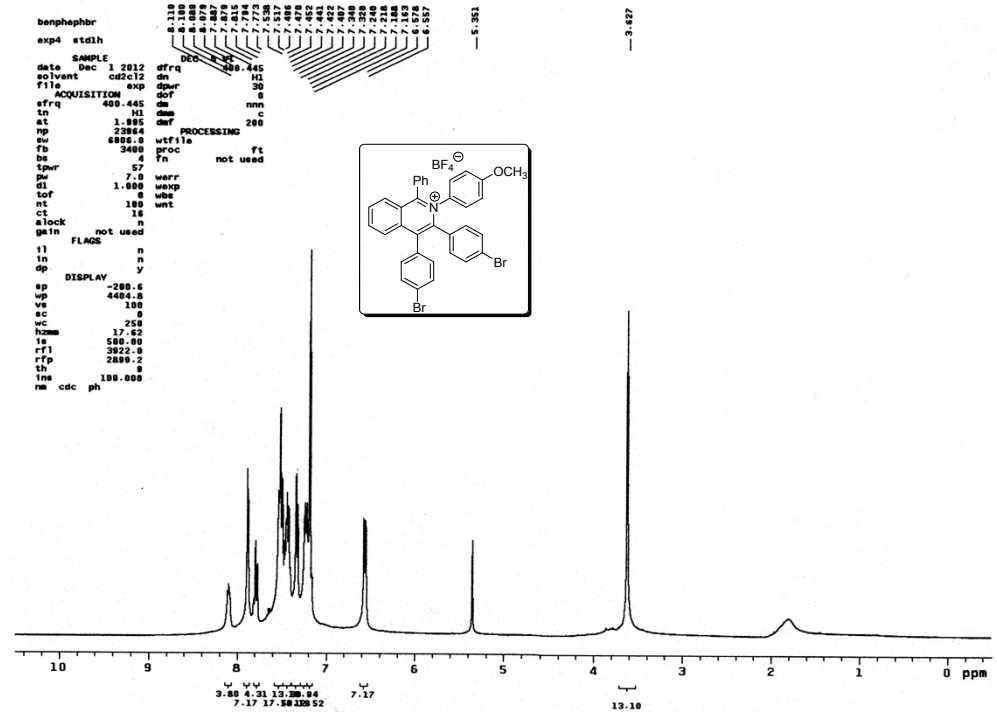


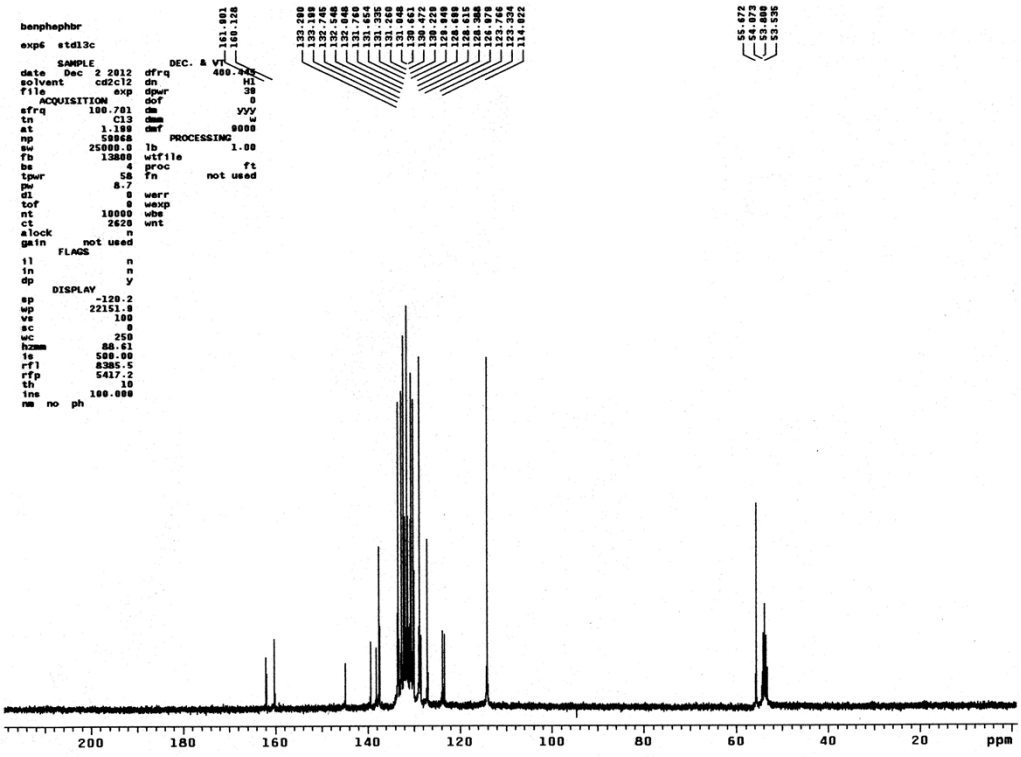


^{1}H and ^{13}C NMR spectra of compound **5ad**.

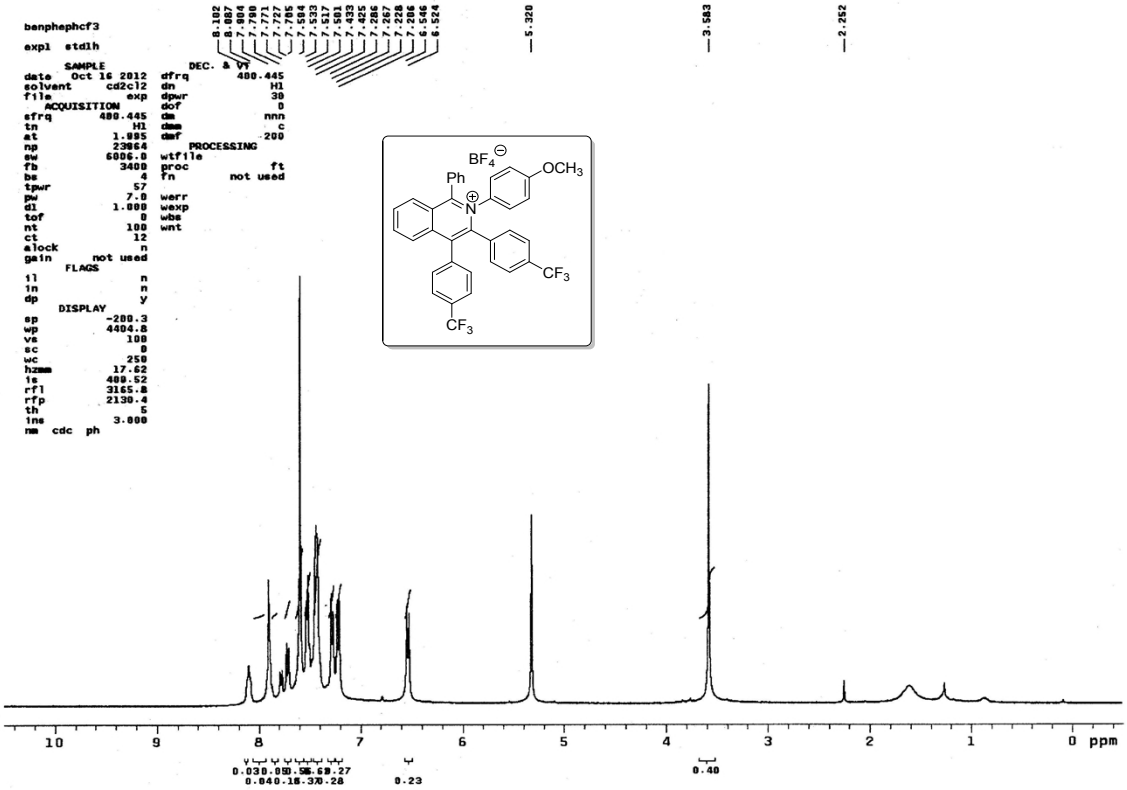


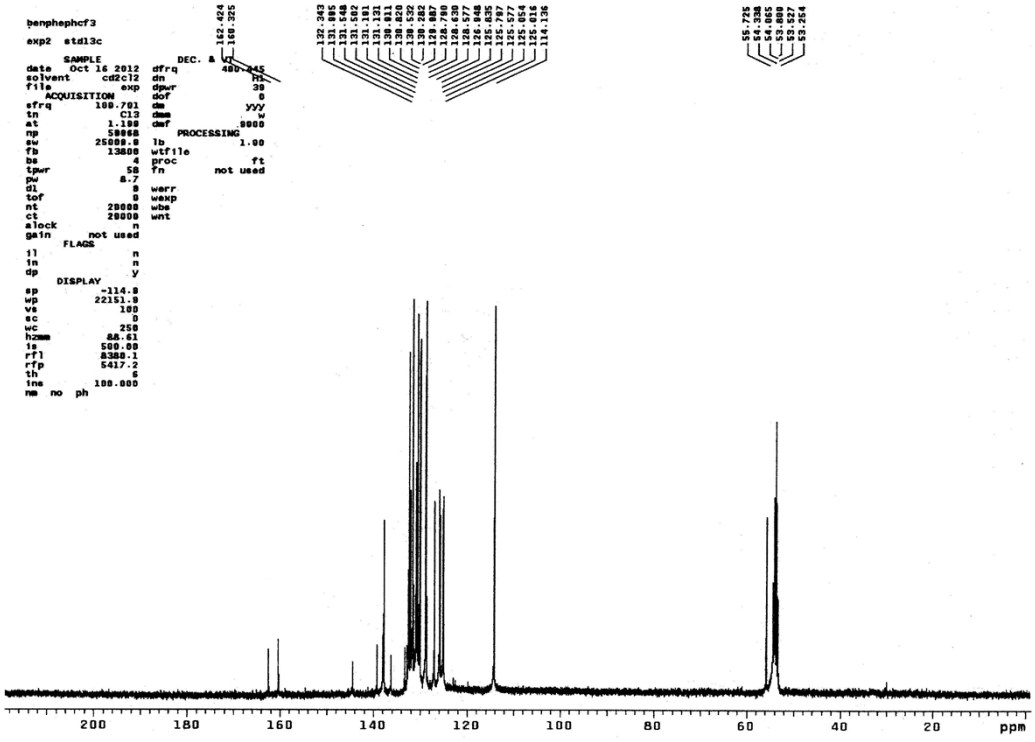
^{1}H and ^{13}C NMR spectra of compound **5ae**.



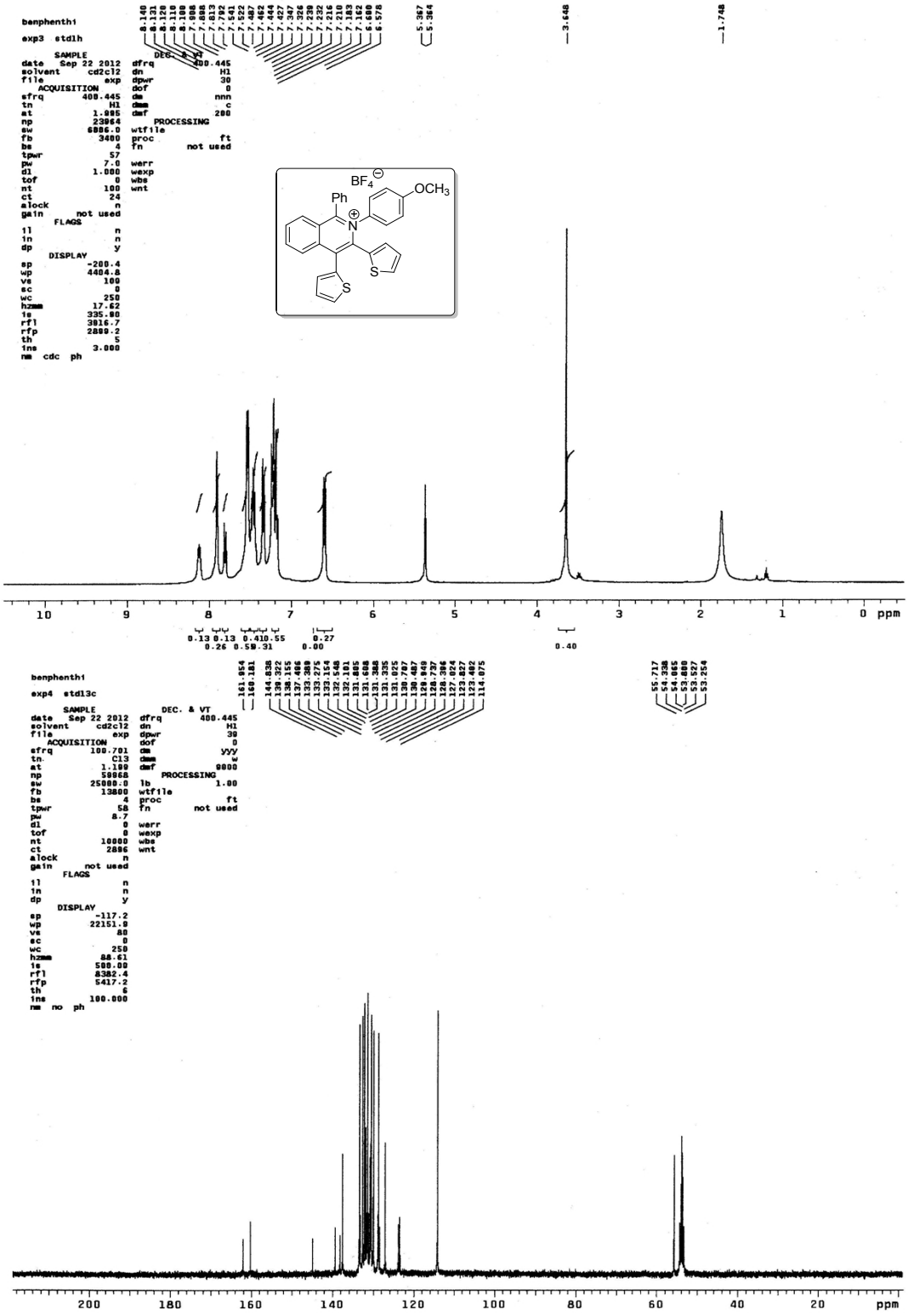


^{1}H and ^{13}C NMR spectra of compound **5af**.

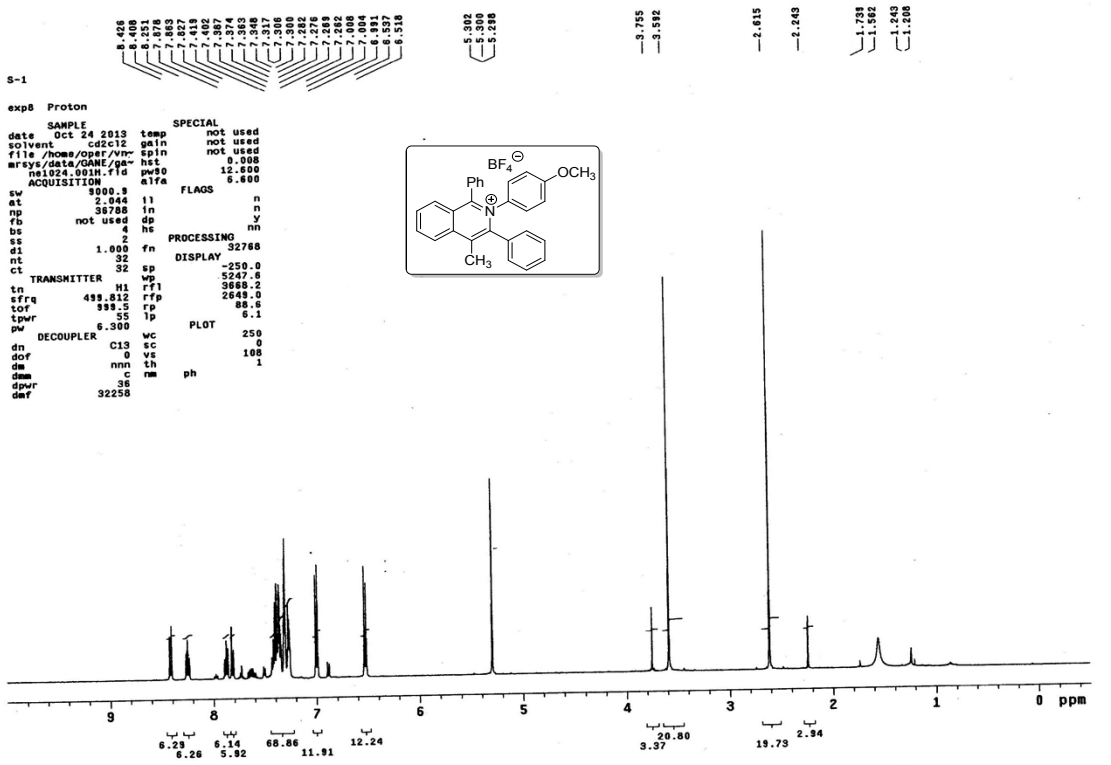


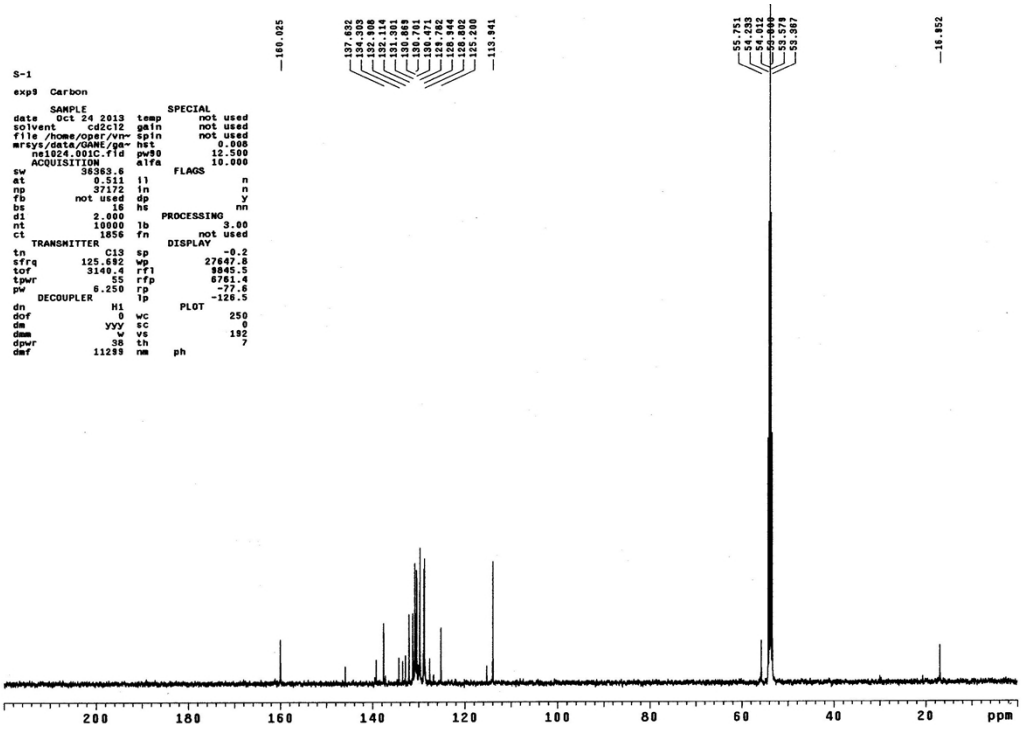


^{1}H and ^{13}C NMR spectra of compound **5ag**.

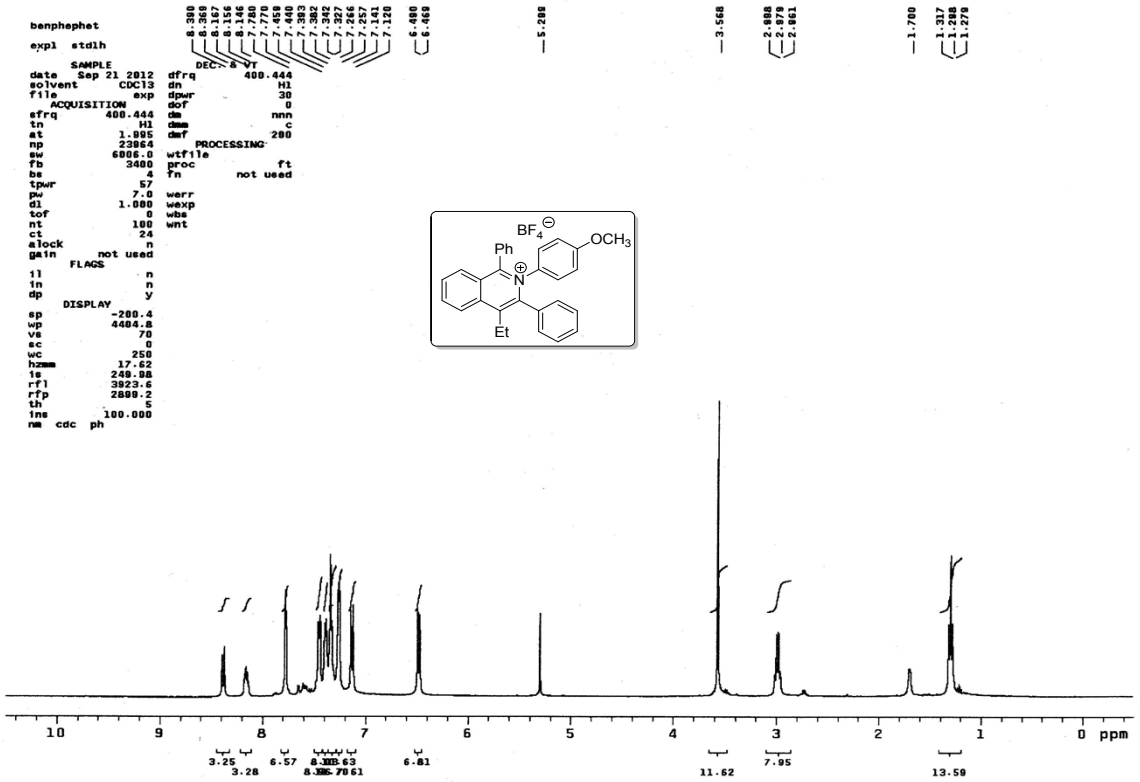


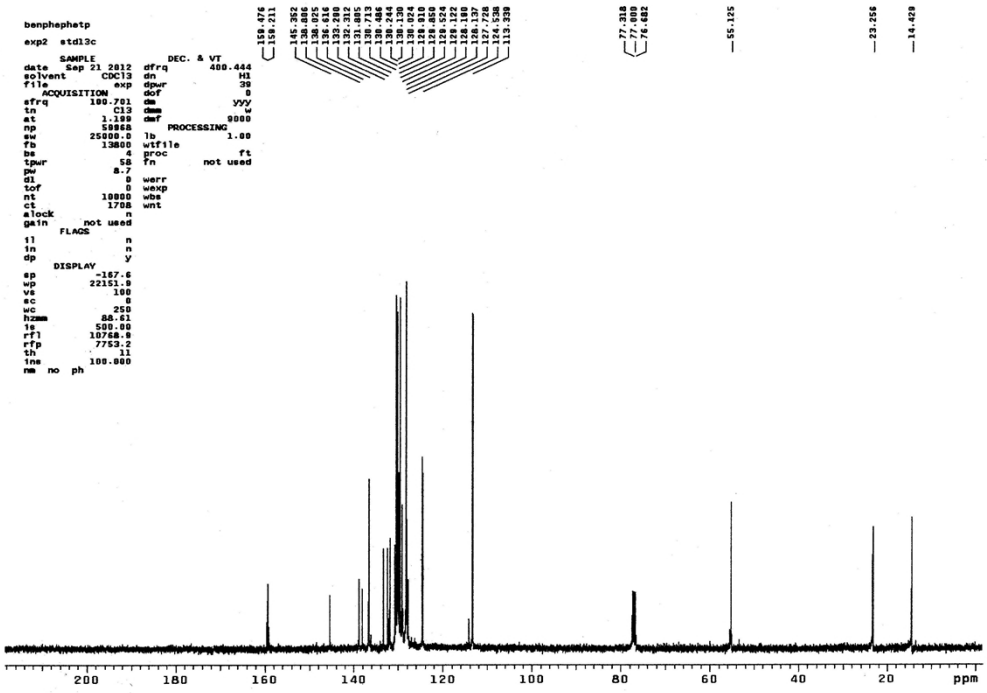
^{1}H and ^{13}C NMR spectra of compound **5ah**.



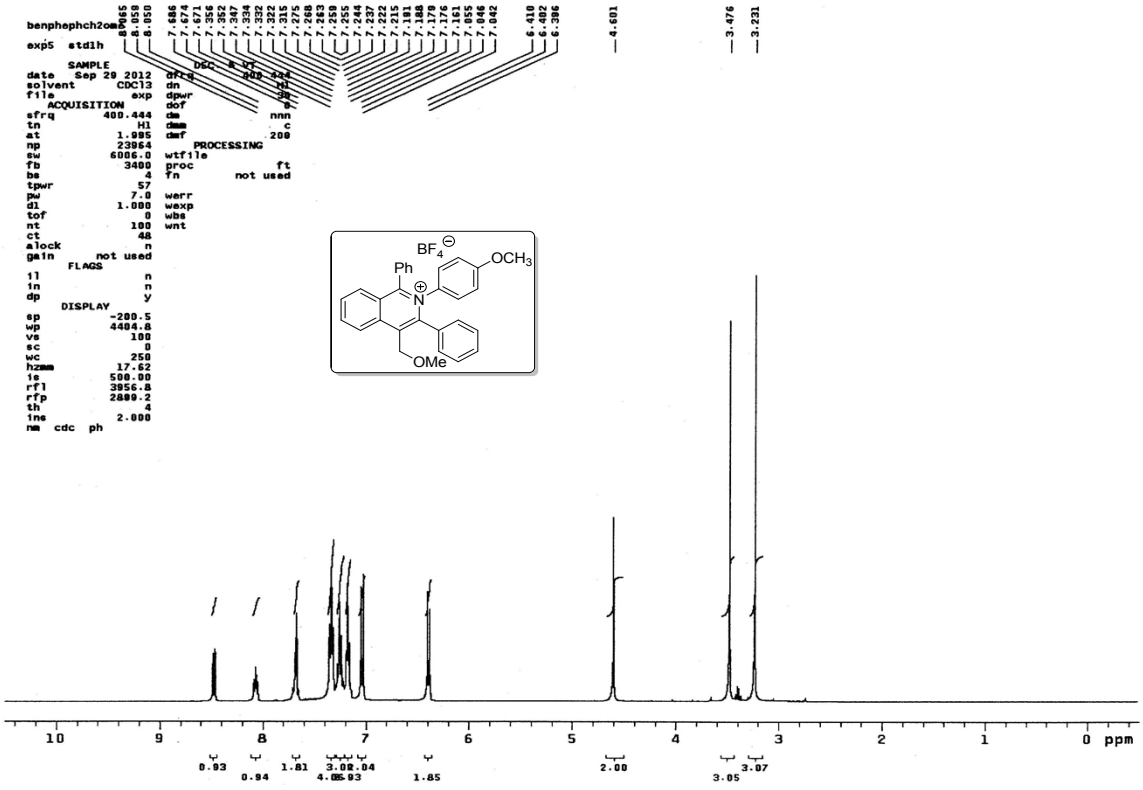


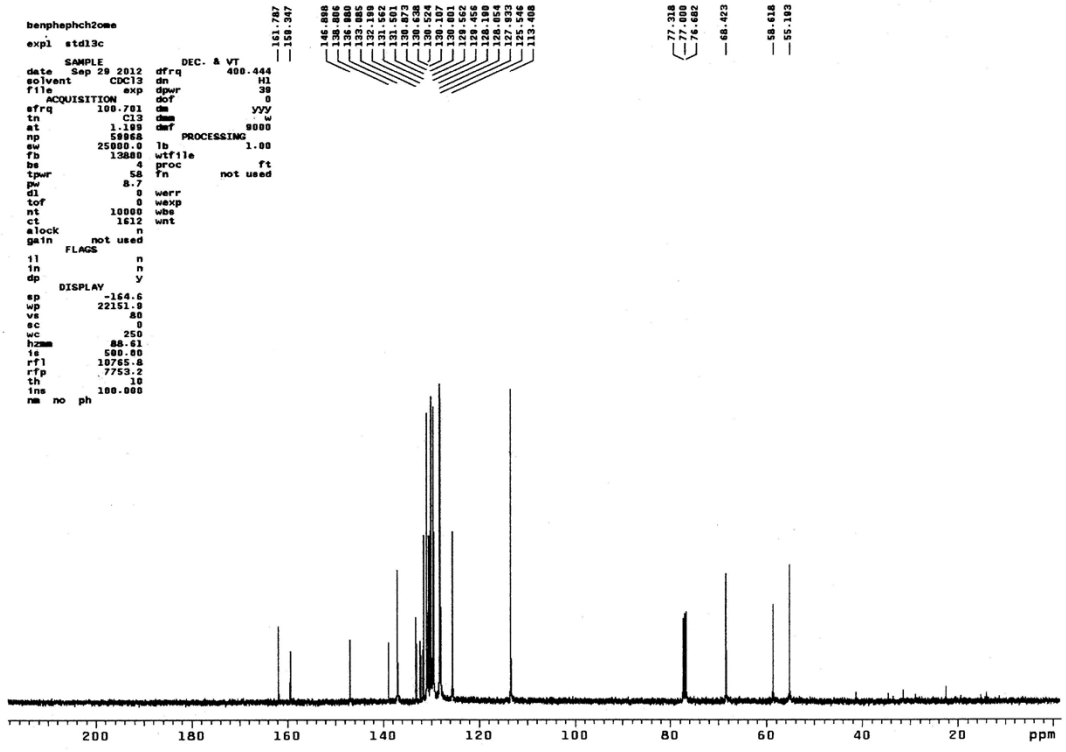
^{1}H and ^{13}C NMR spectra of compound **5ai**.



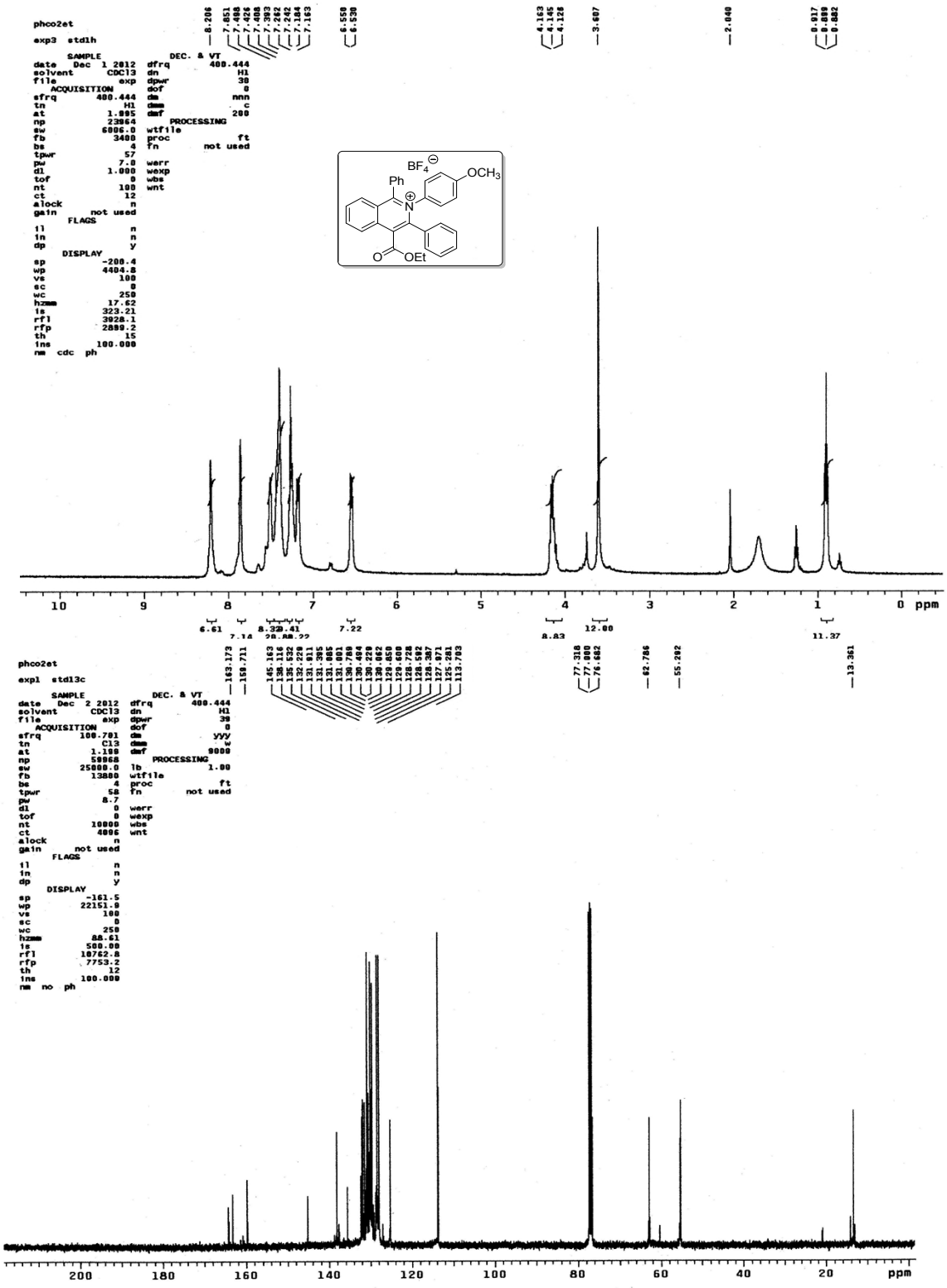


^{1}H and ^{13}C NMR spectra of compound **5aj**.

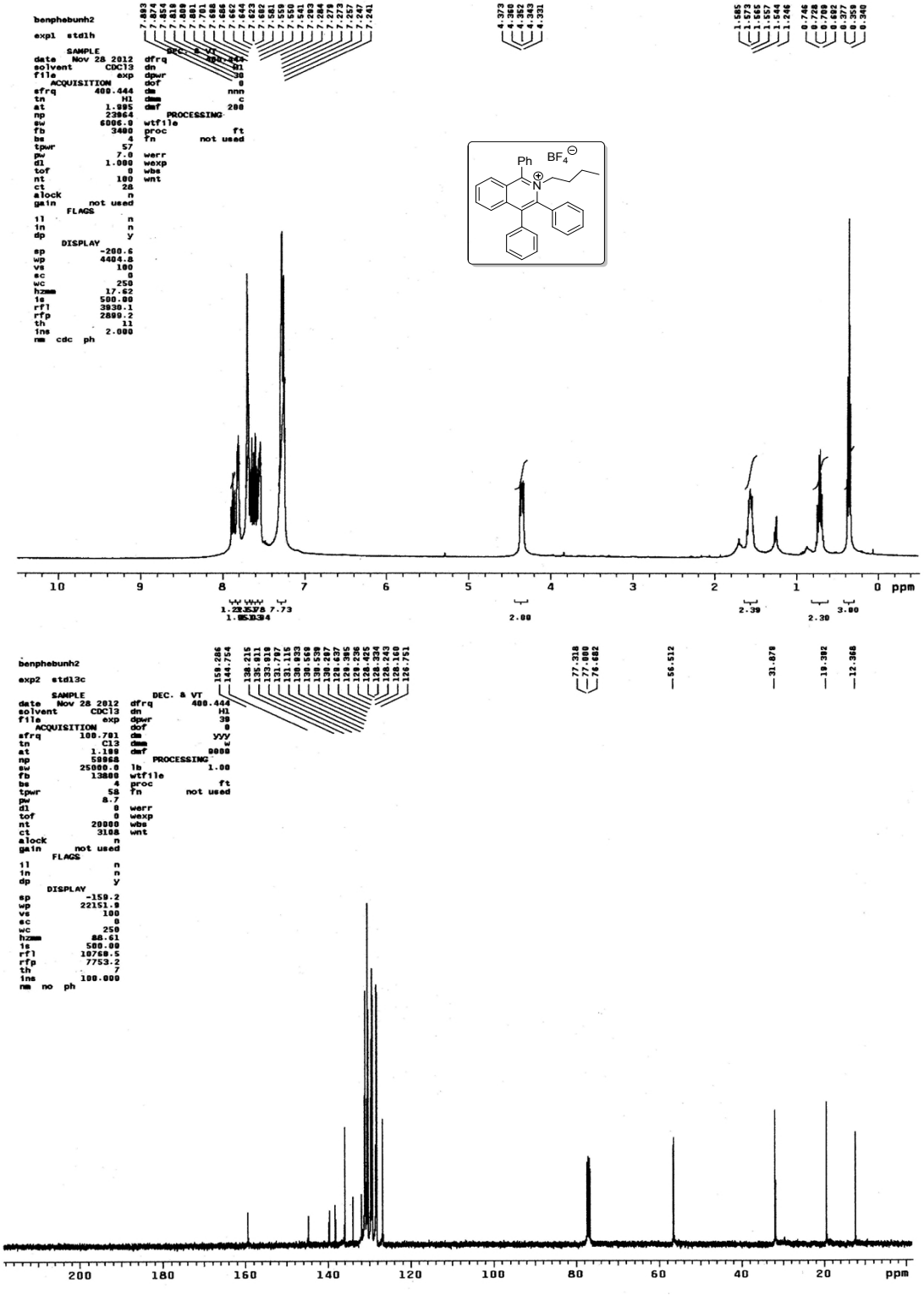




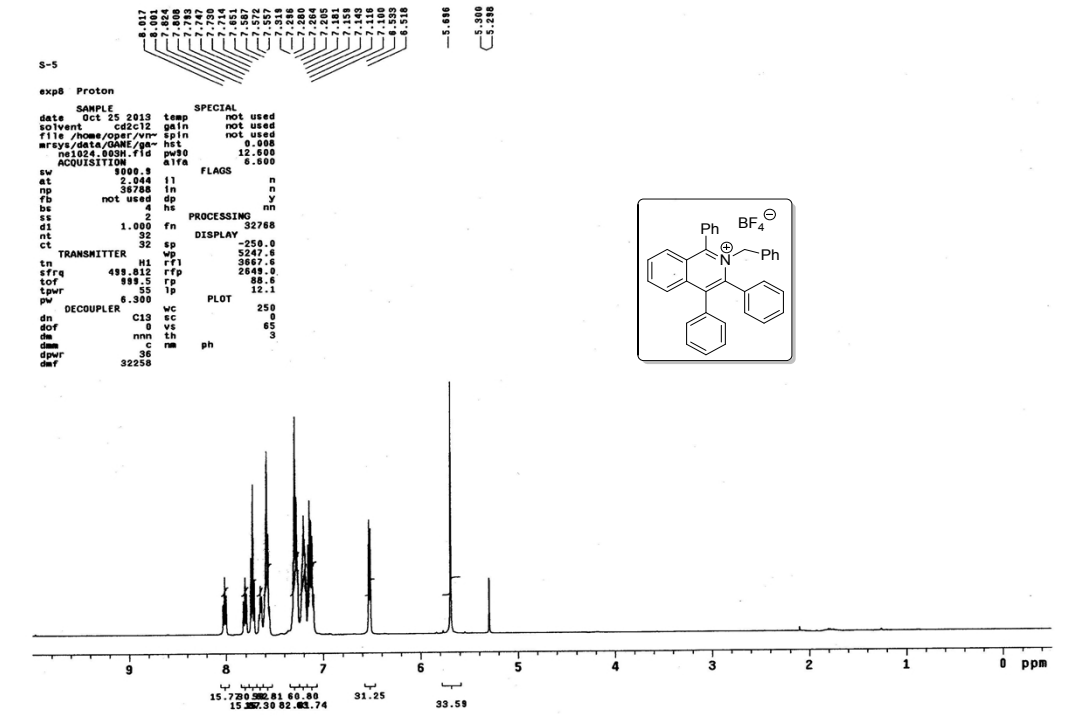
^{1}H and ^{13}C NMR spectra of compound **5ak**.

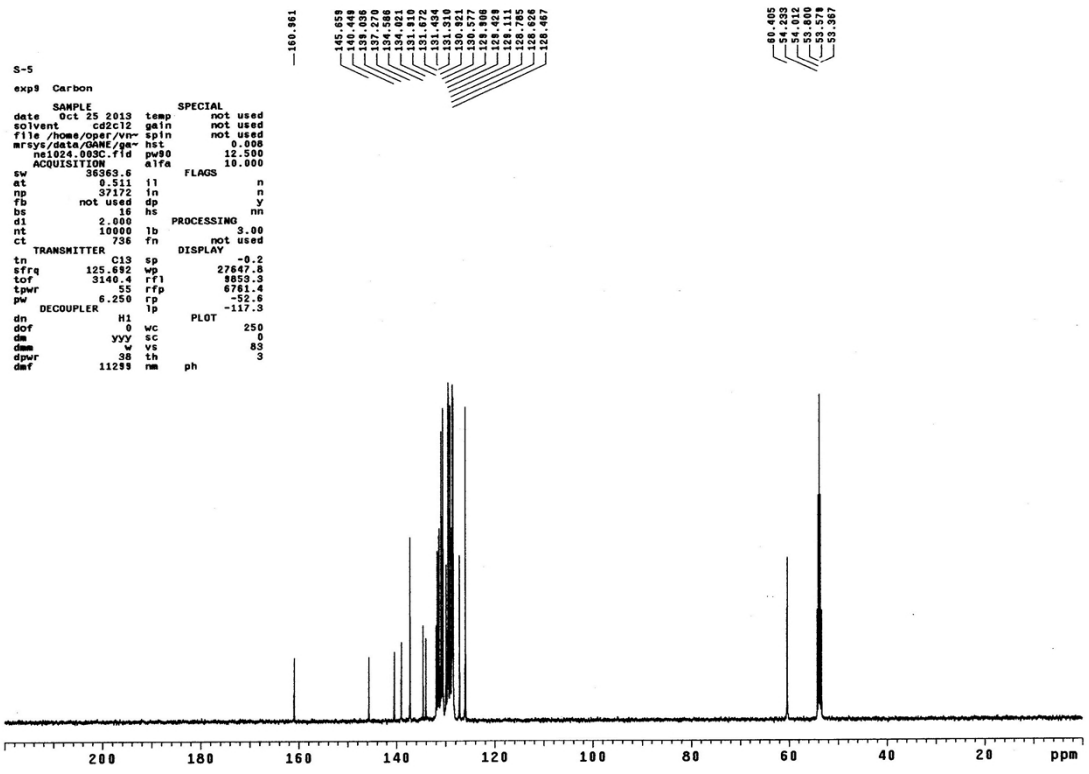


^{1}H and ^{13}C NMR spectra of compound **5ca**.

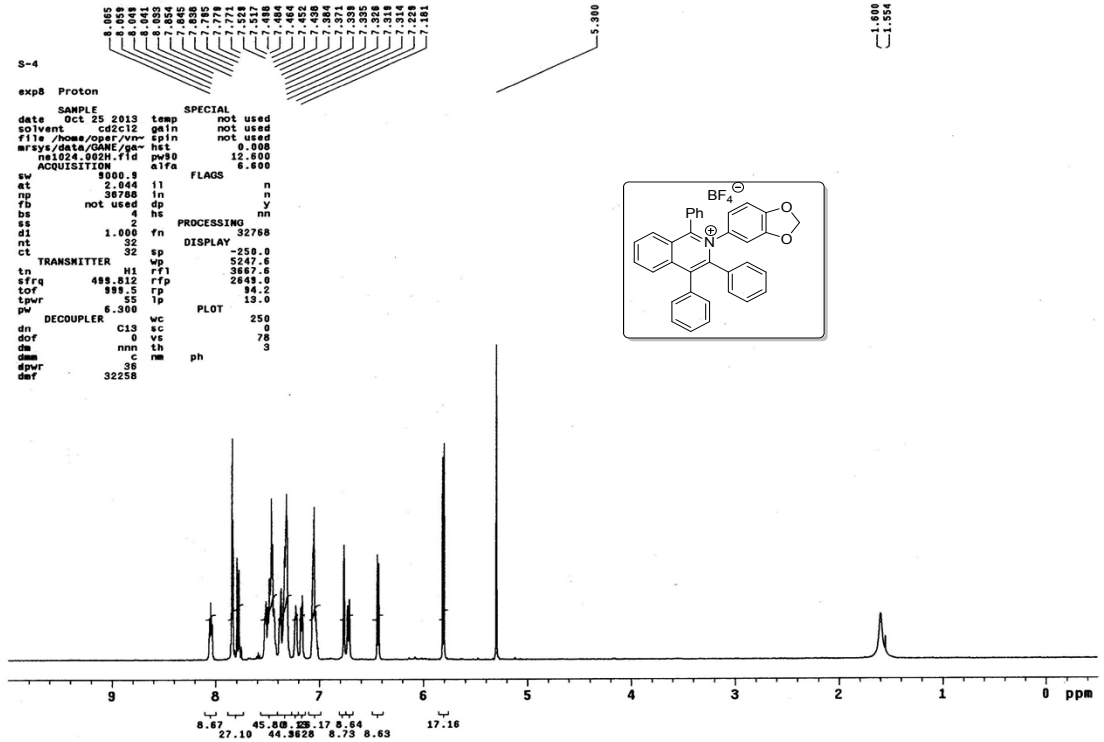


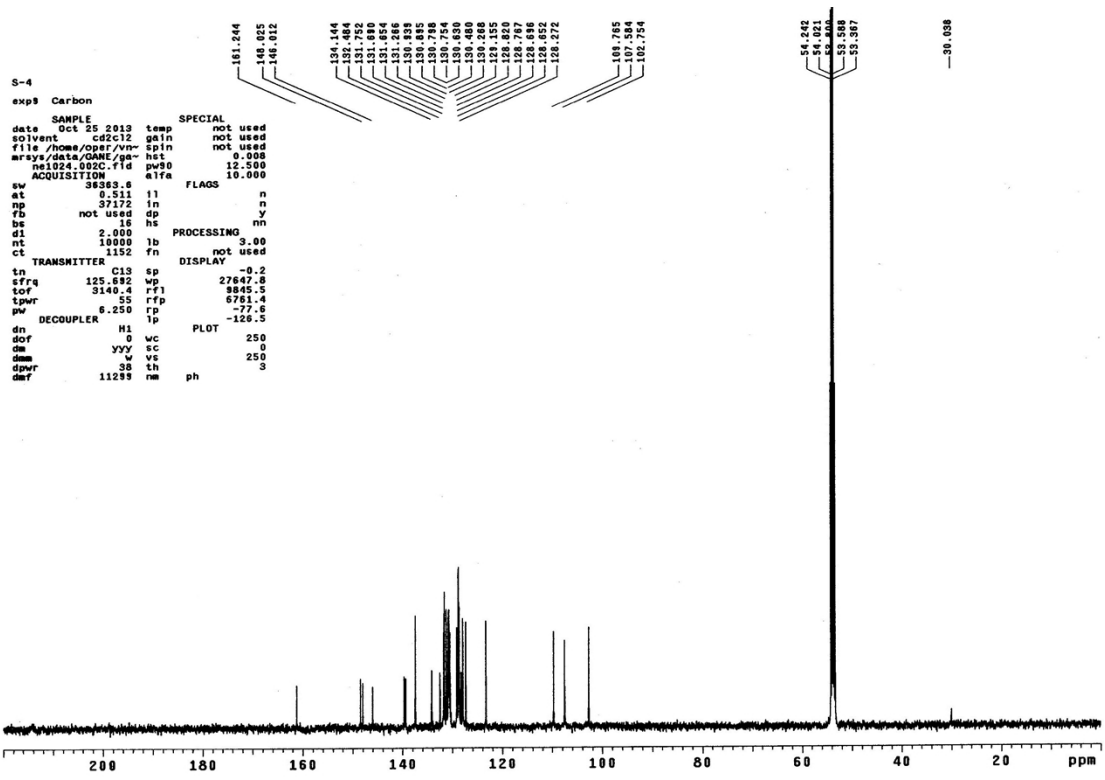
^{1}H and ^{13}C NMR spectra of compound **5da**.



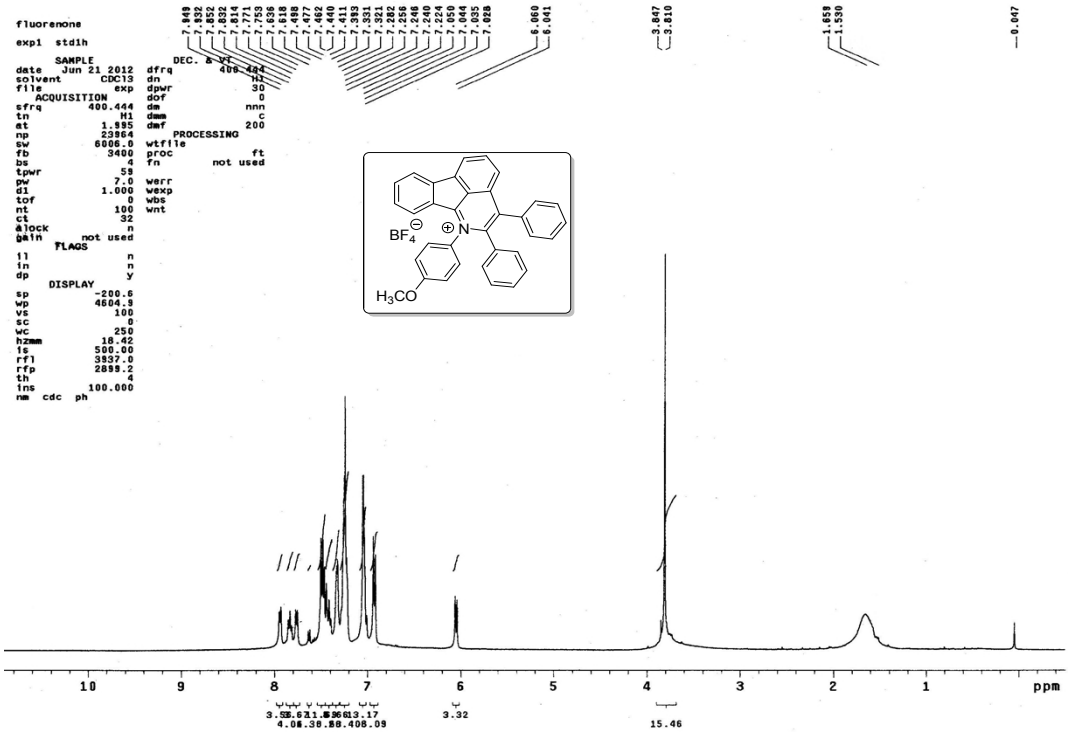


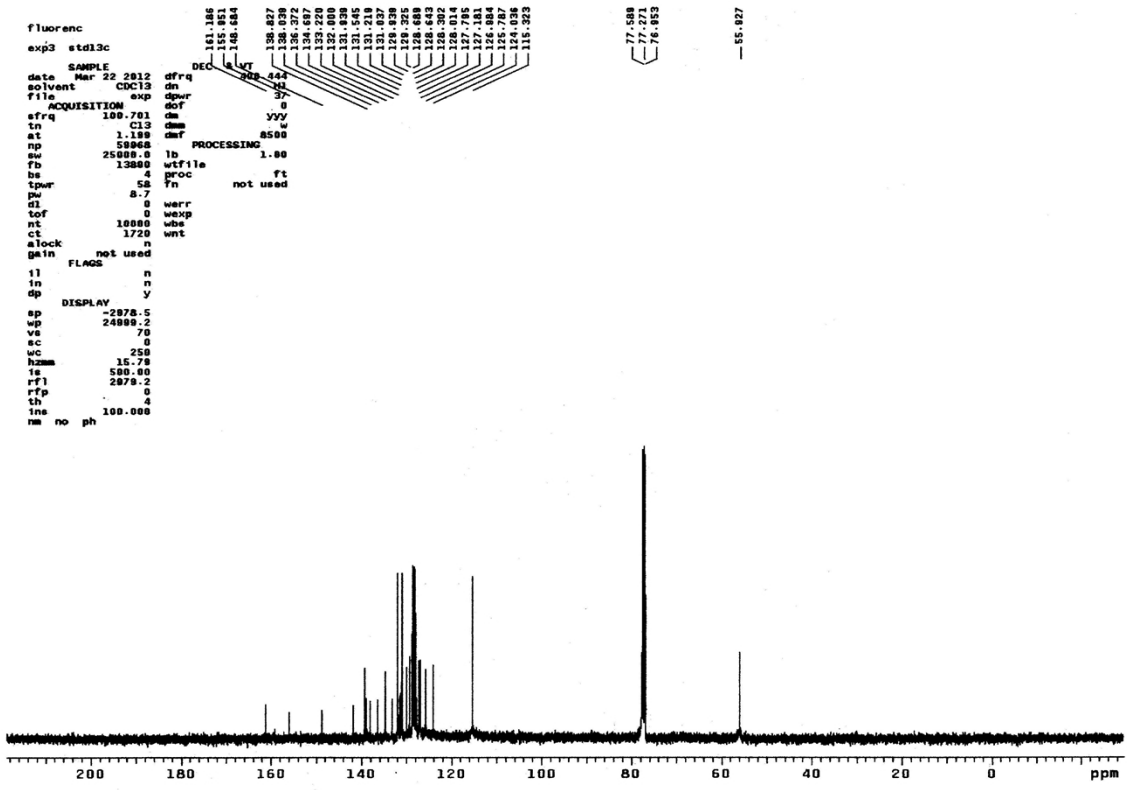
^{1}H and ^{13}C NMR spectra of compound **5ea**.



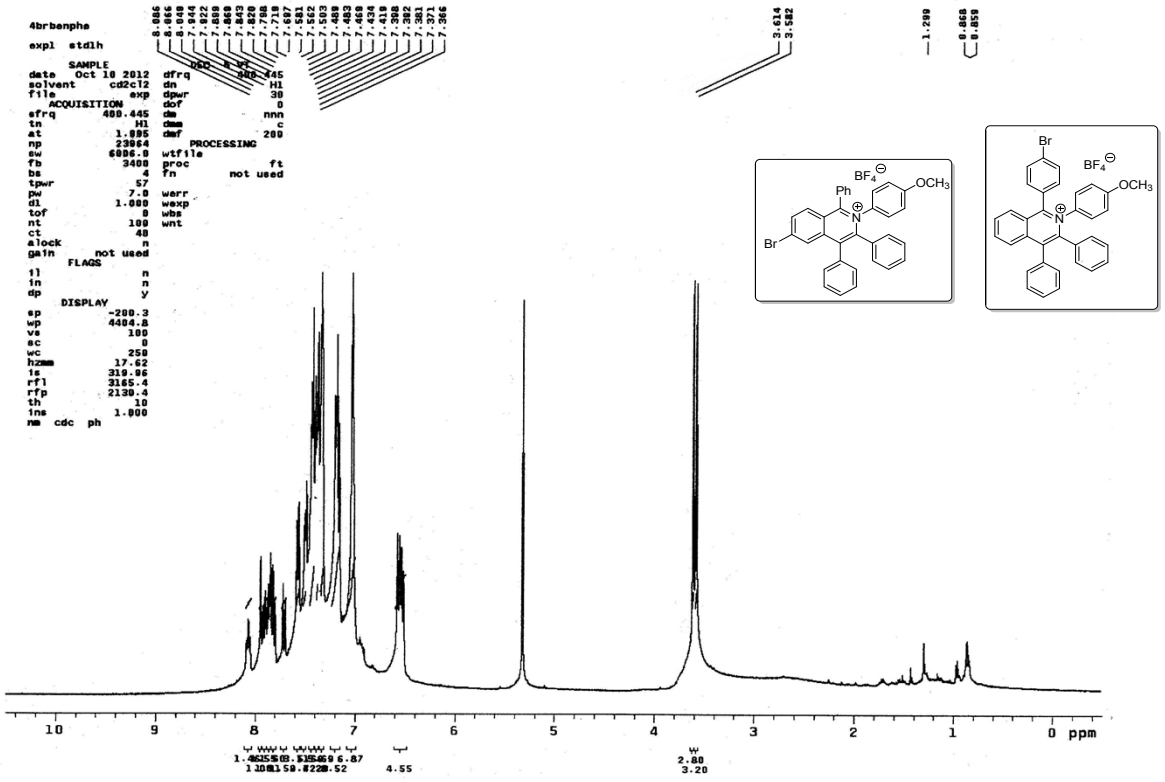


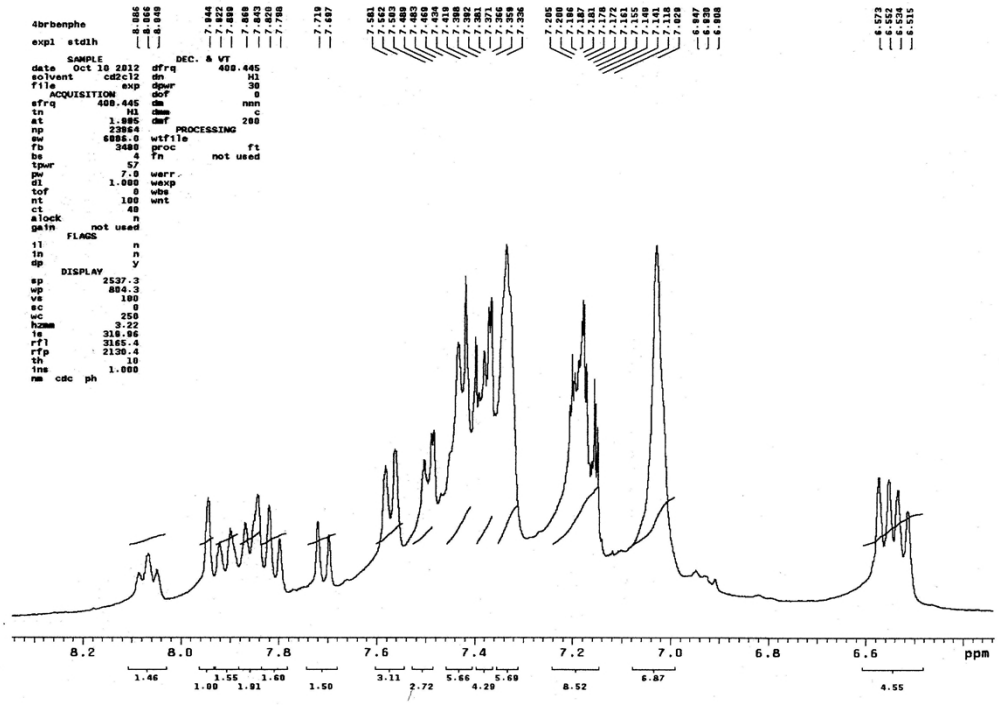
^{1}H and ^{13}C NMR spectra of compound **5fa**.



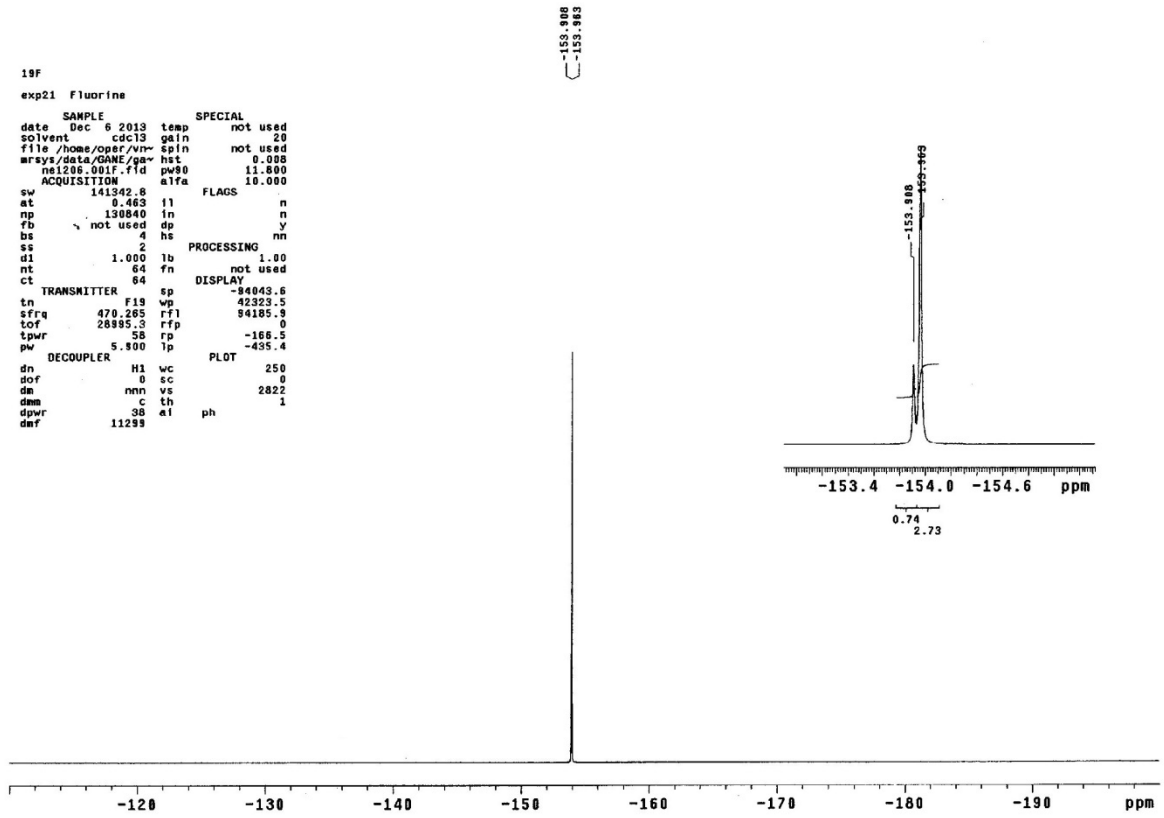


^{1}H and ^{13}C NMR spectra of compound **5ab**.





^{19}F NMR spectrum of **3aa**



^{11}B NMR spectrum of **3aa**